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ROLE OF SPECIATION IN METAL REMOVAL BY ACTIVATED SLUDGE

University — Université
University of Alberta

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée
Ph.D

Year this degree conferred — Année d'obtention de ce grade
1982

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ROLE OF SPECIATION IN METAL REMOVAL BY ACTIVATED SLUDGE

by

Ⓒ JEPPE S. NIELSEN

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR of PHILOSOPHY
IN
ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA
FALL 1982

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To

my wife, Linda

and

my children, Sara and Adam

for

their endless love, understanding, patience and
encouragement during this program

ABSTRACT

The removal of nickel by activated sludge was studied by adopting a mechanistic approach. Nickel was chosen as the metal of interest because it was found to exist mainly in the soluble phase in Edmonton sewage, it was poorly removed by biological treatment, and nickel concentrations in Edmonton sewage were high compared to other large cities in western Canada.

The soluble nature of nickel suggested that it might be largely removed by sorption onto activated sludge. Consideration of the equilibria for the various sorption mechanisms furthermore suggested that free nickel ion concentrations were more relevant than total soluble nickel concentrations.

Batch and a flow through column equilibration methods involving cation exchange were investigated to measure free nickel ion concentrations. Theoretical equations were derived and experimentally verified using synthetic solutions containing 10^{-6} to 10^{-7} M free nickel. Both methods provided accurate results. The batch method requires the use of several weights of resin to compensate for perturbation of the equilibria by the resin. The flow through method is non-perturbing so that each analysis requires only one sample. Measurements of free nickel ion concentrations in sewage were carried out with the flow through method.

Negligible free nickel ion concentrations ($< 3 \times 10^{-8}$ M or $\leq 6\%$ of total soluble nickel concentrations) were measured in Edmonton sewage. Titration of several sewage samples with nickel showed that complexation capacities were about 10^{-5} M (0.6 mg/L Ni). Concentrations of NTA indicated that NTA could be a major ligand for nickel complexation in Edmonton sewage.

Batch experiments were carried out to relate nickel uptake by activated sludge to total soluble nickel and free nickel ion concentrations in sewage samples. The uptake isotherms clearly demonstrated that there was a direct relationship between nickel uptake and free nickel ion concentrations. On the other hand, the isotherms using total soluble nickel concentrations were non-linear over the entire range of initial total soluble nickel concentrations used (up to 1.7×10^{-5} M or 1.0 mg/L).

Equations relating nickel removal from sewage by activated sludge to the free nickel ion concentration in untreated sewage and its position on the complexation capacity curve were derived and applied to experimental results. In contrast to published metal removal models, these equations do not require assumptions about the stoichiometry of nickel-ligand complexes formed in sewage and on activated sludge surfaces.

ACKNOWLEDGEMENTS

This research was supported by a research contract from the Municipal Engineering Branch, Standards and Approvals Division and the Research Management Division of Alberta Environment and a research contract from the Water and Sanitation Department of the City of Edmonton.

I would like to express my sincerest appreciation and thanks to the following people.

My advisors, Dr. Steve Hrudey and Dr. Frederick Cantwell for their expert guidance, advice and enthusiasm throughout this research program.

Messrs. Michel Létourneau, John Ward, Glen Brown and Ken Elstone for help in setting up and carrying out the field investigation at the Edmonton Gold Bar Wastewater Treatment Plant.

Mrs. Valerie Williams, Mr. Karl Toth and Mr. Bill George for assistance with some laboratory work near the end of the research program.

Mr. Tom Casey for his ungrudging help in solving problems with the text processing language (Textform) used to generate this thesis.

Mrs. Linda Nielsen and Mrs. Nola Shaw for typing this document.

Dr. Ian Joliffe and Mrs. Linda Nielsen for such careful proofreading of this thesis.

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GLOSSARY OF ABBREVIATIONS AND SYMBOLS

AAS	atomic absorption spectroscopy
ASV	anodic stripping voltammetry
C_M	total metal concentration
$[M^{2+}]$	free metal ion concentration
COD	chemical oxygen demand
EDTA	ethylenediaminetetraacetic acid
GFAAS	graphite furnace atomic absorption spectroscopy
Ka	acid dissociation constant
K'_L	stability constant (aqueous)
K'_A, K'_S	stability constant (solids)
K_{IE}	ion exchange coefficient
$\underline{M}$	molar (moles/L)
mixed liquor	mixed suspension of activated sludge floc and primary effluent in aeration basin
MLVSS	mixed liquor volatile suspended solids
NTA	nitrilotriacetic acid
TOC	total organic carbon
β_n	overall metal formation constant
λ_o	resin distribution coefficient
λ	resin distribution ratio
λ_o^{SL}	sludge distribution coefficient
θd	mean cell residence time

1. INTRODUCTION

Increasing metals usage and mankind's technological advances are inseparable. As uses of metals for tools, utensils, medicines and agricultural purposes increased, it was inevitable that some of these uses should result in adverse effects to humans. The dramatic increase in metals usage during the twentieth century, together with increasing awareness of environmental and health hazards, have created immense interest in their concentrations and fates in the environment.

Although non-metals such as arsenic are of environmental concern, the so-called "heavy metals" have been of particular interest. Heavy metals are an ill-defined group of elements with specific gravities greater than about four or five, and include cadmium, chromium, cobalt, copper, iron, lead, gold, manganese, mercury, molybdenum, nickel, silver and zinc (Brown and Lester, 1979; International Encyclopedia of Chemical Science, 1964; Lapedes, 1974).

These metals frequently occur in municipal wastewaters, often at concentrations which are considered to be high. Consequently, municipal sewage treatment plants may receive substantial metal loadings. The traditional role of these plants has been to remove organic matter and suspended solids from sewage. However, efficient metals removal is also essential because metals discharged in treated sewage can be toxic to aquatic life or can enter the human food chain through the consumption of crops, fish or water supplies which are contaminated with metals.

Free metal ion (defined as uncomplexed hydrated ions, in contrast to soluble complexed metal forms) concentrations of cadmium, copper, nickel and zinc as low as 10^{-7} to 10^{-8} $\underline{M}$ have been found to be toxic to algae, fish and crustaceans (Allen *et al.*, 1980; Fezy *et al.*, 1979; Pagenkopf *et al.*, 1974; Sunda *et al.*, 1978). Metal toxicities in natural waters have been found to be directly dependent on concentrations of the free metal ions and not on total metal concentrations.

Tragic examples of the effects of water-borne "heavy metals" on human health have even occurred during the last forty years when environmental awareness has been unprecedented. The Japanese Itai-Itai disease, which resulted from the consumption of rice grown in paddy fields irrigated with cadmium-contaminated water, had caused almost 100 deaths up to the end of 1965 (Purves, 1977). Nearly 1000 cases of food poisoning, approximately 100 of which were fatal, occurred among inhabitants near Minamata Bay, Japan, between 1953 and 1973 from eating fish and shellfish contaminated with mercury (D'Itri and D'Itri, 1977). During 1970-71, fish from Lake St. Clair on the Canada-U.S.A. border contained up to fourteen times the mercury limit of 0.5 mg/kg permitted for fish destined for human consumption (Baker and Luh, 1971).

"Heavy metals" may also be toxic to aerobic and anaerobic biological wastewater treatment processes with resultant deteriorations in effluent quality and sludge digestor performance (Barth *et al.*, 1965; Hayes and Theis, 1978; Kugelman and Chin, 1971; Nielsen and Hrudey, 1981). Metal toxicities in activated sludge systems appear to decrease as follows:

(i) Nitrifiers:

Cd > Ni ≥ Cr(VI) > Cu > Hg > Zn > Cr(III)

(ii) Aerobic heterotrophs:

Cu ≥ Ni ≥ Hg > Cd > Pb > Cr(VI) ≥ Zn > Cr(III)

(iii) Anaerobic digestion:

Ni > Cu > Pb > Cr > Zn >> Cd

Nitrifiers have generally been found to be more susceptible to metals toxicity than other activated sludge microorganisms. Influent metal concentrations of 1 to 10 mg/L (as total metal) are required to noticeably affect aerobic activated sludge treatment processes whereas considerably higher concentrations are necessary to inhibit anaerobic processes. These threshold toxic metal concentrations, however, are at least an order of magnitude larger than those normally found in municipal wastewaters. Furthermore, acclimation of activated sludge microorganisms to relatively low baseline metal concentrations increases microbial resistances to metals.

It is obvious that water-borne heavy metals pose severe environmental and health problems. Consequently, guidelines and standards governing maximum and desirable metal concentrations in wastewaters discharged into public sewers, in treated effluents and in drinking water sources and supplies have been widely promulgated.

The following critical literature review to March 1982, discusses cadmium, chromium, copper, lead, mercury, nickel and zinc in municipal wastewaters and their removal by the activated sludge treatment process.

2. LITERATURE REVIEW

2.1 METALS REMOVAL BY MUNICIPAL ACTIVATED SLUDGE TREATMENT PLANTS

Metals are removed at both primary and secondary treatment stages in conventional activated sludge treatment systems.

2.1.1 Metal Removal Processes by Primary Sedimentation

Metals must be either in an insoluble form or attached to settleable solids in order to be removed by sedimentation. The formation of insoluble hydroxides, carbonates and phosphates is possible depending on the composition of the sewage (Carter and McKinney, 1973; Heukelekian and Gellman, 1955; Stoveland *et al.*, 1979a). Lester *et al.* (1979b) found that 50 mg/L concentrations of chromium(VI) and lead were precipitated, probably as the hydroxide and sulphate forms, respectively, when added to growth media containing a high organic concentration (1000 mg/L sucrose).

2.1.2 Metal Removal Processes by Activated Sludge

Secondary treatment removes metals by different mechanisms depending upon the form in which the metal is present.

1. Precipitated or non-settleable particulate metals are removed by entrapment in the floc. There is virtually no mention of these processes in the literature. Apart from mentioning that precipitation would probably occur only in "dead spots" in aeration tanks (as a result of bad design or operation), nothing further will be said about this category of metals removal.

2. Dissolved metals are removed by sorption to activated sludge surfaces and by metabolically-mediated active transport across cellular membranes.

The metal-containing floc is removed by secondary clarification and consequently efficient metals removal is also dependent on efficient final clarification.

2.1.2.1 Nature of Activated Sludge

Activated sludge consists of a complex interacting mixture of bacteria and protozoa together with smaller numbers of fungi, algae and invertebrates (Calaway, 1968; Curds, 1963, 1971, 1975; Hawkes, 1963; McKinney and Gram, 1956; Pike and Curds, 1971; Pipes, 1966). The bacteria are mostly gram negative heterotrophs which include *Zoogloea*, *Pseudomonas*, *Sphaerotilus*, *Azotobacter*, *Flavobacterium*, *Mycobacterium*, *Micrococcus*, *Staphylococcus*, *Bacillus*, *Arthrobacter*, *Nocardia* and *Bdellovibrio*. *Zoogloea* sp. are believed to be the most common. Prosthetic bacteria such as *Caulobacter* and *Hyphomicrobia*, and autotrophic species such as *Nitrosomonas* may also be present. The activated sludge bacteria exist as aggregations or flocs of varying sizes.

Protozoa, which can constitute up to 5% of the mixed liquor volatile suspended solids, MLVSS, consist mainly of free-swimming, crawling or attached ciliates with smaller numbers of amoebae and flagellates. The main species of ciliates are *Vorticella*, *Opercularia* and *Epistylis*, all of which are attached protozoa. Although protozoa perform some removal of organic matter and enhance flocculation, they are believed to function mainly in producing a clear effluent by feeding on dispersed bacteria.

Few fungi usually exist in municipal activated sludge plants. They can predominate under abnormal conditions and filamentous fungi, for example *Geotrichum* sp., can cause sludge bulking. The filamentous bacterium *Sphaerotilus natans* has also been reported to cause bulking although it is now believed that *Geotrichum* has sometimes been wrongly identified as *Sphaerotilus*.

Algae are normally almost non-existent because the highly turbid conditions in activated sludge aeration tanks do not allow penetration of sufficient light to sustain photosynthesis.

Invertebrates are mainly represented by rotifers with fewer numbers of nematodes being present. Rotifers also help to clarify the effluent by feeding on bacteria and small pieces of floc which cannot be ingested by ciliates.

2.1.2.2 Bacterial Extra-Cellular Polymers

Although it was once believed that the only bacterium which could produce extracellular polymers was *Zoogloea ramigera*, it has been shown that a wide variety of gram negative and gram positive species are capable of this activity (Bitton and Freihofer, 1978; Pike and Curds, 1971). Some bacteria can produce many times their dry weight as extracellular polymers (Wilkinson, 1958).

Extracellular polymers in activated sludge occur as insoluble capsules which adhere to cell walls and as a dissolved or colloidal slime which can become detached from the cells. As an example, *Z. ramigera* 115 has an extracellular capsule composed of intermeshed polymer strands containing globular packets of cells (Friedman *et al.*, 1968). The quantities of capsular polymers are normally larger than those of slime polymers (Dugan, 1975; Wilkinson, 1958).

Chemical compositions of capsular polymers, which are similar to those of soluble slime polymers (Forster, 1971), are variable. They always contain a large polysaccharide fraction, which may also vary in composition. The polysaccharides can be low or high molecular weight components consisting of neutral sugars (for example, glucose, galactose, fucose, mannose, ribose and rhamnose), acidic sugars (for example, glucuronic acid) and amino sugars such as N-acetylglucosamine. It does not appear that capsular polymers contain substantial quantities of aromatic fulvic or humic acid components under aerobic conditions (Boyd *et al.*, 1979; Forster, 1971; Friedman *et al.*, 1968; Steiner *et al.*, 1976; Tezuka, 1973; Wilkinson, 1958).

Insoluble extracellular polymers may also contain proteins and lesser amounts of ribonucleic and deoxyribonucleic acids (Sato and Ose, 1980; Tenney and Verhoff, 1973). These components are likely to have been liberated by cellular disintegration, autolysis or damage during severe polymer extraction methods (Brown and Lester, 1979).

2.1.2.3 Metal Removal Processes

1. Sorption processes

Activated sludge has been observed to sorb up to 4% metals on an organic matter weight basis (Cheng *et al.*, 1975; Rudolfs and Zuber, 1953). It is evident that extracellular polymers play an important role in metal uptake. *Z. ramigera* 115, which produces extensive extracellular polymer, was reported to have a very high affinity for copper and zinc ions whereas *Z. ramigera* I-16, which produces little capsular material, had only half the affinity for these metals (Friedman and Dugan, 1968).

Uptake of cadmium, copper, lead, mercury, nickel and zinc, at concentrations of up to 1000 mg/L, by viable activated sludge exhibits an initial rapid phase followed by a long-term slow phase. The initial rapid phase has been measured to last for 3 minutes to 3 hours and can account for at least 90% of the metal uptake (Ayers *et al.*, 1965; Cheng *et al.*, 1975; Lamb and Tollefson, 1973; Mathys, 1979; Nelson *et al.*, 1981; Neufeld and Hermann, 1975). Autoclaved activated sludge was found to have the same initial rates of metal uptake as viable activated sludge but did not show a second slow phase of metal uptake (Cheng *et al.*, 1975; Nelson *et al.*, 1981). These data were interpreted to mean that the initial rapid phase involves attachment to the surfaces of viable and non-viable flocs by physico-chemical sorption processes and that the second slow phase involves incorporation of metals into viable cells by active bacterial uptake. It is also likely that entrapment of precipitated metals or metals associated with non-settleable solids in the biological floc can contribute to the initial rapid phase of metal uptake.

Laboratory observations that the percentage uptake by activated sludge of cadmium, mercury, nickel and zinc decreased with increasing metal concentration suggest saturation of metal uptake sites on floc surfaces (Cheng *et al.*, 1975; Dugan and Pickrum, 1972; Esmond and Petrasek, 1974; Mathys, 1979; Neufeld and Hermann, 1975). Data for metals uptake by activated sludge under laboratory conditions commonly fit Langmuir or Freundlich isotherms (Nelson *et al.*, 1981; Neufeld and Hermann, 1975; Neufeld *et al.*, 1977). Metal removal efficiencies at full scale activated sludge plants have been reported to be both independent of influent metal concentrations (Oliver and

Cosgrove, 1974), and to increase with increasing metal concentrations in sewage influents (Brown *et al.*, 1973). The highest metal concentrations in municipal wastewaters are generally lower than those used in laboratory experiments.

The dynamic nature of metal uptake was first postulated by Moulton and Shumate (1964) and Ayers *et al.* (1965). These investigators observed that the amount of copper sorbed onto the floc decreased if the metal concentration in the activated sludge aeration tank was decreased or if the concentration of uncomplexed ligands was increased by increasing the MLVSS or influent sewage organic strength. It has also been reported that copper was slowly released by activated sludge after the initial rapid uptake phase and that the proportions released increased as the influent metal concentrations were decreased (Lamb and Tollefson, 1973; Moulton and Shumate, 1964).

Sorption of soluble metals to extracellular polymers can potentially occur by cation exchange, complexation with complexing ligands in the floc and by non-polar adsorption forces. These processes can be rapid and result in the establishment of a state of dynamic equilibrium between wastewater metals and those on the sludge.

(i) Cation exchangers are insoluble solid materials which consist of fixed charge sites and mobile counter-ions which can be exchanged reversibly for a stoichiometrically equivalent amount of cations from the surrounding solution (Helfferich, 1962). Evidence for ion exchange as one of the uptake mechanisms was presented by Dugan and Pickrum (1972) who found that *Z. ramigera* 115 released potassium ions as various other metallic ions were taken up by the floc.

(ii) Complexes may be defined in a general manner as species formed by association of two or more simpler species, each of which is capable of independent existence (Rossotti and Rossotti, 1961). Cations in aqueous solution are coordinated with water molecules which may be replaced by other ligand(s), the extent of replacement being governed by the relative stabilities of the aquo and complex species.

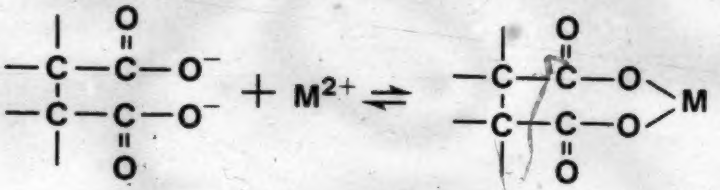
Two types of complex species can be distinguished (Stumm and Brauner, 1975). Outer sphere species or ion pairs occur when the metal ion and/or the ligand retain some of their coordinated water molecules upon complex formation. Bonding is by long range electrostatic forces and the resulting stability constants are relatively small. Inner sphere species or complexes arise when the interacting ligand(s) is immediately adjacent to the metal cation. For these, short range or covalent forces contribute to the bonding and stability constants tend to be greater. In this connection, uptake of metals has been found to promote the settleability of activated sludge and this has been ascribed to displacement of bound water from the sludge by the metals (Forster and Lewin, 1972; Rudolfs and Zuber, 1953).

In contrast to soil solutions and natural waters, little is known about metal complexation with activated sludge. The relative absence of aromatics suggests that the predominant metal complexation sites might be hydroxyl and carboxylic groups of polysaccharide molecules.

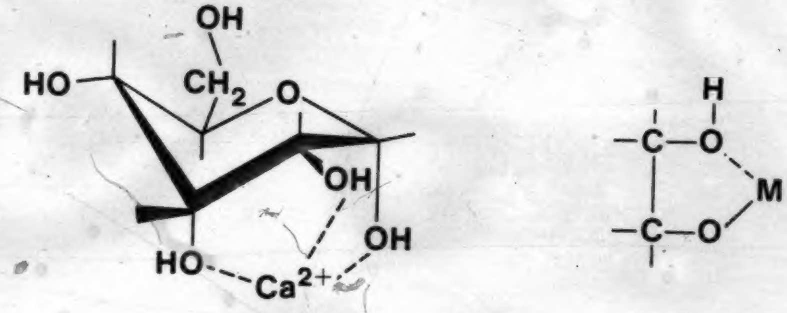
Forster and Lewin (1972) found that uptake of copper by *Z. ramigera* I-16 (which produces limited capsular material) followed the Langmuir isotherm, meaning that there was progressively less chance of sorption sites being available as more metal was sorbed. It was suggested that metal uptake occurred by complexation with carboxyl groups which, at normal physiological pH values, would be practically irreversible. This type of bonding was subsequently repostulated by Steiner *et al.* (1976). The process is illustrated in Figure 2.1(i) for complexation by carboxyl groups in humic acids (Gamble *et al.*, 1970). Carboxyl groups are almost completely ionized at pH values of about 7 (Harper, 1975). Gould *et al.*, (1976) have suggested that strong chelation in the solid state may also involve ring oxygens in polysaccharide molecules.

Metal uptake by the capsule forming *Z. ramigera* 115, on the other hand, exhibited irregular Langmuir, Freundlich and Temkin isotherms. It was postulated that the metals preferentially formed irreversible bonds with carboxyl groups. When these sites were fully occupied, the metals were presumed to form weak electrostatic bonds with hydroxyl groups of the hexose and pentose rings in neutral sugars acting alone or together (Forster and Lewin, 1972; Steiner *et al.*, 1976). Neutral polysaccharides are known to form weak complexes with cations in neutral or acid solutions.

(i) Strong complexation by carboxyl groups (Gamble *et al.*, 1970)



(ii) Weak complexes formed by hydroxyl groups (Rendleman, 1978)



(a) Non-alkaline solutions (b) Alkaline

Figure 2.1 Complex Formation of Metals with Carboxyl and Hydroxyl Groups

The affinity for cations increases as the pH increases due to loss of hydroxyl protons (Rendleman, 1978). This type of complex formation also involves a chelation mechanism between cations and two or more hydroxyl groups in a favourable steric arrangement (Figure 2.1(ii)). Municipal sewage is generally slightly alkaline due to carbonate-bicarbonate buffering.

Metal complexation might also occur with uncharged ligands such as amines or ammonia on the surface of the floc. However, there is no evidence that this mechanism occurs with activated sludge.

(iii) Non-polar adsorption would involve the attachment by non-Coulombic forces of metal-organic molecules to the sludge. This mechanism has not been described in the literature for metals uptake by activated sludge.

2. Active bacterial uptake

The general ability of living organisms to concentrate metals is well documented (Patrick and Loutit, 1976). Work with various bacterial species has shown that metals are mainly associated with cell walls and cell membranes, and not with the cytoplasm (Corpe, 1975; Tornabene and Edwards, 1972). Metal binding sites within cell walls are much stronger than those at cell wall surfaces and it appears that these internal sites undergo metal exchange reactions relatively slowly and can become saturated (Frausto da Silva and Williams, 1976).

Cheng *et al*. (1975) compared nickel uptake by viable and non-active sludge and found that total nickel uptake for the viable sludge was somewhat greater than for the non-active sludge. The nickel remaining in solution also decreased, apparently linearly, between 10 and 60 minutes, whereas uptake by the non-active sludge was independent of time. These results suggested active nickel uptake by the viable sludge which did not occur for the non-active sludge. Mathys (1979) has also reported that activated sludge exhibited a two-stage uptake pattern with cadmium. The second, which started after 24 hours, indicated active processes. Nelson *et al*. (1981), however, found that for cadmium and zinc, viable and autoclaved activated sludge had similar adsorption isotherms whereas for copper, autoclaving decreased uptake.

Although aerobic heterotrophs such as *E. coli* and *Pseudomonas sp.* can metabolize lead and mercury by methylation (Higgins and Burns, 1975; McEntire and Neufeld, 1975; Wong *et al*., 1975) and can eliminate mercury(II) species by reduction to elemental mercury (Furukawa and Tonomura, 1971; Summers and Silver, 1972), the occurrence of these and other types of metabolic transformation mechanisms for metals in activated sludge has not been reported.

2.1.3 Metal Concentrations in Activated Sludge Treatment Plants

The main contributing sources of metals in municipal wastewaters are domestic water supplies, residential wastewaters, commercial and industrial discharges and surface runoff (Atkins and Hawley, 1978; Cheremisinoff and Habib, 1972; Davis and Jacknow, 1975; Gurnham *et al.*, 1979; Klein *et al.*, 1974; Koch *et al.*, 1977).

It has been suggested by Davis and Jacknow (1975) that there seem to be background concentrations of metals in municipal wastewaters in the U.S.A. from non-industrial sectors that may prove to be essentially uncontrollable. Other work from New York City has shown that 84% of cadmium, 80% of chromium, 91% of copper, 38% of nickel and 94% of zinc would continue to be discharged if all industry in the city could achieve zero wastewater discharge (Klein *et al.*, 1974). Gurnham *et al.* (1979) found that foods and household commodities such as detergents, soaps, bleaches, fabric softeners and toilet and facial tissues can contain very high concentrations (up to several hundred p.p.m.) of some metals. These authors found that one-third to one-half of the cadmium, chromium, copper, mercury and zinc in Chicago residential sewage was derived from foods.

In contrast to the foregoing, industrial sources have been found to be the major contributors of metals in some Canadian municipal wastewaters. Oliver and Cosgrove (1975) found that metal loadings to a treatment plant in Southern

Ontario which received about equal flow proportions of residential and industrial wastewaters were generally at least ten times higher than those to a plant receiving only residential sewage. Data from Vancouver showed that cadmium, lead, mercury, nickel and zinc concentrations were higher in mixed wastewaters than in sewage from purely residential areas (Koch *et al*., 1977).

Influent metal concentrations to municipal sewage treatment plants can exhibit large temporal variations because of factors such as water treatment, community affluence, relative magnitudes of domestic, commercial and industrial water uses and climatic conditions.

Cadmium, chromium, copper and nickel inputs to the Dallas White Rock Sewage Plant in Texas were found to arrive as slugs whereas lead exhibited little diurnal variation. The temporal pattern for copper was distinct from the random patterns of the other metals. This indicated a source of copper which was removed from the general location of other sources or a plant which was operating a different work cycle (Weeks, 1975).

In Hawaii, zinc concentrations in raw sewage during a weekend varied directly with sewage flows and showed the greatest diurnal variation of the metals determined. They were greatest during late morning, mid-afternoon and early evening, suggesting that much of the zinc was of domestic origin (Nomura and Young, 1974).

Hourly sampling at a conventional activated sludge plant in Ontario showed that metal inputs were not continuous but consisted of random slugs. Several of the metals had coincident curves indicating that they arose from the same industrial source (Oliver and Cosgrove, 1974).

Dry weather metal concentrations and loadings in municipal wastewaters sampled in Vancouver showed distinct diurnal patterns (Koch *et al.*, 1977). Peaks occurred during peak flows at mid-day and lows occurred during low sewage flows in the early morning. This relationship suggested that metals were associated with particulate matter which settled out in the sewers during low flows and was flushed out during higher flows. Alternately, the coincidence of high flows and high concentrations could simply have reflected inputs from domestic, commercial and industrial metal sources during peak flows with lower metal inputs occurring during off-peak hours.

Daytime metal concentrations in the influent to an activated sludge plant in Zurich, Switzerland, were three to five times higher than night-time values. The metal loadings, particularly for lead, increased sharply during wet weather suggesting urban runoff or scouring of sediment deposits in sewers as major sources (Roberts *et al.*, 1977).

Recent work in Britain has also shown that particularly large temporal variations occurred in the 24-hour inputs of cadmium, copper, lead and zinc to the Oxford Sewage Treatment Works (Lester *et al.*, 1979a; Stoveland *et al.*, 1979a).

Tables 2-1 to 2-7 summarize total metal concentrations that have been measured in pilot and full scale activated sludge treatment plants. The full scale plants serve municipalities with populations ranging from a few thousand to about 500 000 and with varying proportions of commercial and industrial activities.

Of the metals considered, zinc appears to be the most prevalent in municipal sewage followed by chromium, copper, nickel and lead. Concentrations of these metals seldom exceed 0.5 mg/L. Cadmium and mercury occur at concentrations at least one order of magnitude smaller.

High metal concentrations in wastewaters and sludges have been reported from many localities, particularly in the U.S.A. and Britain. The Ontario values are, however, consistently high on a world basis. These high values probably result from relatively high proportions of industrial wastes in municipal sewage. Chromium concentrations in the Edmonton samples also appear to be high.

2.1.4 Metal Removal Efficiencies

The reported work on removal of metals by activated sludge treatment processes falls into two broad categories.

1. The first and largest category involves studies in which total metal concentrations have been measured in the influent to laboratory, pilot and full-scale treatment

TABLE 2.1 Cadmium Concentrations in Municipal Activated Sludge Treatment Plants

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(0.013)		(0.008)		Esmond and Petrasek, 1974
	0.0111		0.0047-0.0065		Stoveland and Lester, 1980
	(5)-(10)		(2.30)-(4.34)		Weber and Sherrard, 1980
Full scale					
Chicago, U.S.A.				66*	Patterson et al., 1975
Chicago, U.S.A.	(0)-(0.077)		(0)-(0.007)	(10)-(296)*	Lue-Hing et al., 1978
Chicago, U.S.A.	0-1.970				Gurnham et al., 1979
Connecticut, New Jersey & New York, U.S.A.	<0.02-0.06		<0.02-6.4		Mytelka et al., 1973
Dallas, U.S.A.	0.055				Weeks, 1975
Hawaii, U.S.A.	0.05-0.065	0.03-0.12	0.02-0.10	1.70-2.20	Nomura and Young, 1974
Indiana, U.S.A.	(0.0328)		(0.00631)	(377)	Yost et al., 1981
Los Angeles, U.S.A.		0.028	0.010	110*	Chen et al., 1974
Michigan, U.S.A.				2-1100*	Page, 1974
Nebraska, U.S.A.	(0.018)		(0.016)		Brown et al., 1973
New York, U.S.A.	0.005-0.046		0.003-0.020	0.4-9.8*	Klein et al., 1974
Ohio, U.S.A.	0.04-0.1	0.02-0.1	0.01		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.021)	(0.018)	(0.007)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				20-460*	Cunningham et al., 1975
Calgary, Canada	0		0		McIntosh, 1980a
Calgary, Canada	0-0.009		0-0.004		McIntosh, 1980b
Edmonton, Canada				23*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.03)	(0.03)	(<0.03)		Brown, 1979a
Edmonton, Canada	(0.03)	(<0.05)	(<0.05)		Brown, 1979b
Edmonton, Canada	0-0.034		0.002-0.065	0.149-0.377	Brown, 1980
Ontario, Canada	0-0.5	0-0.4	0-0.4	0-10	Abbott, 1971
Ontario, Canada				5-45*	Van Loon and Lichwa, 1973
Ontario, Canada	0.003-0.02	0.002-0.01	<0.001-0.005	1.3-3.6*	Oliver and Cosgrove, 1974
Ontario, Canada	0.006-0.04	0.003-0.02	0.001-0.01	2.6-150*	Oliver and Cosgrove, 1975
Ontario, Canada	<0.01-0.15		<0.01	<0.01-1.5	Atkins and Hawley, 1978
60 plants, Germany			0.0005-0.010		Mathys, 1979
Zurich, Switzerland	(0.005)		(0.003)	(30)*	Roberts et al., 1977
Oxford, U.K.	0-0.012	0-0.012	0-0.006	0-120*	Lewin and Rowell, 1973
Oxford, U.K.	0.004-0.008	0.001-0.002	0.001-0.002		Lester et al., 1979a

( ) arithmetic mean

TABLE 2.2 Chromium Concentrations in Municipal Activated Sludge Treatment Plants (continued)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(4.1)	(3.5)	(2.7)	(88.1)	Barth et al., 1964
	(50)	(47)		(420)	Barth et al., 1965
	(15)		(8.4)		Barth et al., 1965
	(0.55)-(15)		(0.20)-(0.7)		Bailey et al., 1970
	(2)-(10)		(0.2)-(6.07)		Wheatland et al, 1971
	(0.215)		(0.093)		Esmond and Petrasek, 1974
	70-152	4.4-38	0.1-5.5		Atwell and Wyman, 1977
	0.108		0.086-0.087		Stoveland and Lester, 1980

TABLE 2.2 Chromium Concentrations in Municipal Activated Sludge Treatment Plants (concluded)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Full scale					
Chicago, U.S.A.	0-0.760				Gurnham et al., 1979
Connecticut, New Jersey & New York, U.S.A.	<0.05-3.80		<0.05-6.80		Mytelka et al., 1973
Dallas, U.S.A.	0.060				Weeks, 1975
Hawaii, U.S.A.	0.012-0.018	0.010-0.030	0.008-0.020	0.44-0.84	Nomura and Young, 1974
Indiana, U.S.A.	0.91-2.38		0		Erganian, 1960
Indiana, U.S.A.	(0.786)		(0.0167)	(1060)	Yost et al., 1981
Indiana, Michigan & Ohio, U.S.A.	0.2-5.6	0.3-6.3	0.01-3.8	88-386	U.S.P.H.S., 1965
Los Angeles, U.S.A.		0.300	0.060	1700*	Chen et al., 1974
Maine, U.S.A.	65-129		2.5-44		Atwell and Wyman, 1977
Muncie, U.S.A.	(0.24)-(0.27)		(0.04)-(0.06)		Davis and Jacknow, 1975
Michigan, U.S.A.				22-9600*	Page, 1974
Nebraska, U.S.A.	(0.059)		(0.013)		Brown et al., 1973
New York, U.S.A.	0.04-0.50		0.03-0.19	13-74*	Klein et al., 1974
Ohio, U.S.A.	0.51-1.07	0.30-0.93	0.14-0.28	66-3200	Tarvin, 1956
Ohio, U.S.A.	0.13-0.54	0.13-0.17	0.07		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.095)	(0.079)	(0.031)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				1600-28,850*	Cunningham et al., 1975
Calgary, Canada	0.002-0.044		0-0.036		McIntosh, 1980a
Calgary, Canada	0.023-1.33		0.007-0.093		McIntosh, 1980b
Edmonton, Canada				2000*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.51)	(0.46)	(0.22)		Brown, 1979a
Edmonton, Canada	(0.66)	(0.26)	(0.12)		Brown, 1979b
Edmonton, Canada	0-6.29		0-0.28	20.27-58.54	Brown, 1980
Ontario, Canada	0-5.0	0-2.0	0-0.64	0.3-220	Abbott, 1971
Ontario, Canada				60-16000*	Van Loon and Lichwa, 1973
Ontario, Canada	0.01-1.64	0.03-0.80	<0.02-0.68	43-310*	Oliver and Cosgrove, 1974
Ontario, Canada	0.02-1.4	0.02-1.0	0.01-0.71	21-3800*	Oliver and Cosgrove, 1975
Ontario, Canada	<0.02-7.9		<0.02-0.24	<0.02-300	Atkins and Hawley, 1978
Winnipeg, Canada	(0.471)			2200*	Carroll and Lee, 1977
60 plants, Germany			0.001-0.100		Mathys, 1979
Zurich, Switzerland	(0.09)		(0.03)	(500)*	Roberts et al., 1977
Salford, U.K.	0.32-1.21				Stones, 1955
Oxford, U.K.	0.05-0.08	0.03	0.02		Stoveland et al., 1979a

( ) arithmetic mean

TABLE 2.3 Copper Concentrations in Municipal Activated Sludge Treatment Plants (continued)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(0.48)	(0.40)	(0.19)	(22.3)	Barth et al., 1964
	(10)	(9)		(196)	Barth et al., 1965
	(10)-(25)	(1.76)-(3.10)	(0.53)-(1.27)		McDermott et al., 1963a
	(0.4)-(5)	(0.19)-(2.65)	(0.10)-(1)		McDermott et al., 1963a
	(2)-(10)		(0.12)-(0.44)		Wheatland et al., 1971
	(0.092)		(0.062)		Esmond and Petrasek, 1974
	0.121		0.090-0.121		Stoveland and Lester, 1980

TABLE 2.3 Copper Concentrations in Municipal Activated Sludge Treatment Plants (concluded)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Full scale					
Chicago, U.S.A.				290*	Patterson et al., 1975
Chicago, U.S.A.	0.2.54				Gurnham et al., 1979
Connecticut, New Jersey & New York, U.S.A.	<0.02-1.30		<0.02-1.50		Mytelka et al., 1973
Dallas, U.S.A.	0-0.97				Weeks, 1975
Hawaii, U.S.A.	0.062-0.09	0.05-0.16	0.01-0.11	8.50-12.00	Nomura and Young, 1974
Indiana, U.S.A.	(0.168)		(0.0252)	(1790)	Yost et al., 1981
Indiana, Michigan & Ohio, U.S.A.	0.1-3.7	0.1-2.8	0.03-3.2	27-88	U.S.P.H.S., 1965
Los Angeles, U.S.A.		0.130	0.040	1500*	Chen et al., 1974
Michigan, U.S.A.				260-10 400*	Page, 1974
Muncie, U.S.A.	(0.25)-(0.26)		(0.06)-(0.08)		Davis and Jacknow, 1975
Nebraska, U.S.A.	(0.170)		(0.067)		Brown et al., 1973
New York, U.S.A.	0.13-0.43		0.10-0.19	45-124*	Klein et al., 1974
Ohio, U.S.A.	0.17-0.69	0.22-0.34	0.05-0.26	382-3200	Tarvin, 1956
Ohio, U.S.A.	0.04-0.12	0.06-0.09	0.02		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.127)	(0.098)	(0.056)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				599-1880*	Cunningham et al., 1975
Calgary, Canada	0.051-0.143		0-0.039		McIntosh, 1980a
Calgary, Canada	0.059-0.176		0.006-0.032		McIntosh, 1980b
Edmonton, Canada				400*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.22)	(0.15)	(0.10)		Brown, 1979a
Edmonton, Canada	(0.20)	(0.11)	(0.07)		Brown, 1979b
Edmonton, Canada	0.03-0.18		0.01-0.03	6.44-12.80	Brown, 1980
Ontario, Canada	0-4.7	0-1.7	0-4.0	1.5-440	Abbott, 1971
Ontario, Canada				300-2400*	Van Loon and Lichwa, 1973
Ontario, Canada	0.06-0.98	0.04-0.66	0.01-0.22	50-430*	Oliver and Cosgrove, 1974
Ontario, Canada	0.06-1.20	0.06-0.77	0.02-0.20	420-3200*	Oliver and Cosgrove, 1975
Ontario, Canada	0.08-1.7		<0.01-4.3	2.2-87	Atkins and Hawley, 1978
Winnipeg, Canada	(0.157)			522*	Carroll and Lee, 1977
Zurich, Switzerland	(0.12)		(0.06)	(800)*	Roberts et al., 1977
Salford, U.K.	0.33-0.78				Stones, 1958
Oxford, U.K.	0.28-0.60	0.06-0.33	0-0.016	600-1800*	Lewin and Rowell, 1973
Oxford, U.K.	0.032-0.219	0.010-0.093	0.001-0.011		Lester et al., 1979a

( ) arithmetic mean

TABLE 2.4 Lead Concentrations in Municipal Activated Sludge Treatment Plants

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(0.095)		(0.042)		Esmond and Petrasek, 1974
	0.109		0.058-0.074		Stoveland and Lester, 1980
Full scale					
Chicago, U.S.A.				512*	Patterson et al., 1975
Chicago, U.S.A.	0-0.610				Gurnham et al., 1979
Connecticut, New Uersey & New York, U.S.A.	<0.20-0.60		<0.20-0.20		Mytelka et al., 1973
Dallas, U.S.A.	0-0.28				Weeks, 1975
Hawaii, U.S.A.	0.04-0.07	0.02-0.06	0.01-0.04	3.00-3.95	Nomura and Young, 1974
Indiana, U.S.A.	(0.0507)		(0.00255)	(94.0)	Yost et al., 1981
Los Angeles, U.S.A.		0.110	0.042	760*	Chen et al., 1974
Michigan, U.S.A.				240-12,400*	Page, 1974
Muncie, U.S.A.	(0.92)-(0.93)		(0.17)-(0.27)		Davis and Jacknow, 1975
Nebraska, U.S.A.	(0.160)		(0.092)		Brown et al., 1973
Ohio, U.S.A.	0.28	0.19	0.21		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.119)	(0.055)	(0.022)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				620-1800*	Cunningham et al., 1975
Calgary, Canada	0.008-0.168		0-0.075		McIntosh, 1980a
Calgary, Canada	0.020-0.470		0-0.045		McIntosh, 1980b
Edmonton, Canada				420*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.62)	(0.57)	(0.52)		Brown, 1979a
Edmonton, Canada	(<0.4)	(<0.4)	(<0.4)		Brown, 1979b
Edmonton, Canada	0-0.162		0-0.108	3.45-10.97	Brown, 1980
Ontario, Canada	0-0.8	0-1.1	0-0.35	0-200	Abbott, 1971
Ontario, Canada				185-1425*	Van Loon and Lichwa, 1973
Ontario, Canada	0.04-1.16	0.01-0.49	0.001-0.05	42-220*	Oliver and Cosgrove, 1974
Ontario, Canada	<0.05-1.1	<0.05-0.5	<0.05-0.2	<1.3-5900*	Oliver and Cosgrove, 1975
Ontario, Canada	<0.01-1.2		<0.01-0.03	0.6-96	Atkins and Hawley, 1978
Winnipeg, Canada	(0.184)			675*	Carroll and Lee, 1977
60 plants, Germany			0.0008-0.25		Mathys, 1979
Zurich, Switzerland	(0.14)		(0.05)	(800)*	Roberts et al., 1977
Salford, U.K.	0.48-0.78				Stones, 1960
Oxford, U.K.	0.42-1.20	0.04-0.40	0.02-0.23	1190-3010*	Lewin and Rowell, 1973
Oxford, U.K.	0.081-0.250	0.020-0.060	0.001-0.028		Lester et al., 1979a

( ) arithmetic mean

TABLE 2.5 Mercury Concentrations in Municipal Activated Sludge Treatment Plants

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	5-10		2.45-4.17		Ghosh and Zugger, 1973
	(0.00051)		(0.00016)		Esmond and Petrasek, 1974
Full scale					
Chicago, U.S.A.	0-0.0007				Gurnham et al., 1979
Connecticut,	<0.0001-0.0680		<0.0001-0.1250		Mytelka et al., 1973
New Jersey,					
New York, U.S.A.					
Dallas, U.S.A.	0-0.212				Weeks, 1975
Hawaii, U.S.A.	0.0004-0.0011	0.0002-0.0014	0-0.0002	0.096-0.175	Nomura and Young, 1974
Los Angeles, U.S.A.		0.00049	0.00012	7.4*	Chen et al., 1974
Nebraska, U.S.A.	(0.0006)		(0.0005)		Brown et al., 1973
Wisconsin, U.S.A.				5-12*	Cunningham et al., 1975
Edmonton, Canada				6*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.0108)	(0.0046)	(0.008)		Brown, 1979a
Edmonton, Canada	(0.0042)	(0.0048)	(0.0039)		Brown, 1979b
Ontario, Canada	0-0.01		0-0.01		Abbott, 1971
Ontario, Canada	<0.001-0.020	<0.001-0.009	<0.001-0.001	0.46-1.10*	Oliver and Cosgrove, 1974
Ontario, Canada	<0.001-0.007	<0.001-0.003	<0.001-0.005	0.89-15*	Oliver and Cosgrove, 1975
Ontario, Canada	0.0001-0.0098		<0.00003-0.00015	0.0043-0.074	Atkins and Hawley, 1978

( ) arithmetic mean

TABLE 2.6 Nickel Concentrations in Municipal Activated Sludge Treatment Plants

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(2.0)	(1.6)	(1.3)	35.7	Barth et al., 1964
	(1)-(10)	(0.97)-(8.2)	(0.75)-(7.2)	<71	McDermott et al., 1965
	(2)-(10)		(0.67)-(3.7)		Wheatland et al., 1971
	(0.073)		(0.058)		Esmond and Petrasek, 1974
	0.111		0.078-0.103		Stoveland and Lester, 1980
Full scale					
Chicago, U.S.A.	0-1.20				Gurnham et al., 1979
Connecticut, New Jersey & New York, U.S.A.	<0.10-1.00		<0.10-0.80		Mytelka et al., 1973
Dallas, U.S.A.	0-0.26				Weeks, 1975
Hawaii, U.S.A.	0.06-0.07	0.06-0.25	0.04-0.18	0.75-1.33	Nomura and Young, 1974
Indiana, U.S.A.	(0.115)		(0.0812)	(533)	Yost et al., 1981
Indiana, Michigan & Ohio, U.S.A.	0.01-3.5	0.01-2.9	0.01-2.5	2-97	U.S.P.H.S., 1965
Los Angeles, U.S.A.		0.200	0.149	410*	Chen et al., 1974
Michigan, U.S.A.				14-1440*	Page, 1974
Muncie, U.S.A.	(0.12)-(0.14)		(0.09)-(0.12)		Davis and Jacknow, 1975
New York, U.S.A.	0.05-0.31		0.04-0.26	3.3-24.4*	Klein et al., 1974
Ohio, U.S.A.	0.05-0.38	0.15-0.40	0.10-0.21	150-610	Tarvin, 1956
Ohio, U.S.A.	0.19-0.28	0.12-0.21	0.23		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.078)	(0.077)	(0.070)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				240-1700*	Cunningham et al., 1975
Calgary, Canada	0-0.020		0-0.018		McIntosh, 1980a
Calgary, Canada	0-0.054		0-0.006		McIntosh, 1980b
Edmonton, Canada				160*	Dudas and Pawluk, 1975
Edmonton, Canada	0-0.132		0-0.106	1.28-2.84	Brown, 1980
Ontario, Canada	0-12	0-2.4	0-2.0	0-116	Abbott, 1971
Ontario, Canada				25-170*	Van Loon and Lichwa, 1973
Ontario, Canada	<0.03-1.89	<0.03-1.6	<0.03-0.72	12-120*	Oliver and Cosgrove, 1974
Ontario, Canada	<0.03-1.8	0.03-1.4	0.03-1.0	13-780*	Oliver and Cosgrove, 1975
Ontario, Canada	0.01-4.5		<0.01-0.23	0-84	Atkins and Hawley, 1978
Winnipeg, Canada	(0.066)			64*	Carroll and Lee, 1977
Zurich, Switzerland	(0.08)		(0.05)	(300)*	Roberts et al., 1977
Salford, U.K.	0.12-0.31				Stones, 1959a
Oxford, U.K.	0.03-0.05	0.02-0.04	0.01-0.02		Stoveland et al., 1979a

( ) arithmetic mean

TABLE 2.7 Zinc Concentrations in Municipal Activated Sludge Treatment Plants (continued)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Pilot/Laboratory scale					
	(2.5)-(10)	(2.05)-(19.8)	(0.12)-(5.16)	<342	McDermott et al., 1963b
	(2.7)	(2.0)	(0.26)	122	Barth et al., 1964
	(2)-(10)		(0.08)-(0.26)		Wheatland et al., 1971
	(0.320)		(0.112)		Esmond and Petrasek, 1974
	0.60		0.39-0.45		Stoveland and Lester, 1980

TABLE 2.7 Zinc Concentrations in Municipal Activated Sludge Treatment Plants (concluded)

TYPE/LOCATION	CONCENTRATION (mg/L or *mg/kg dry wt)				REFERENCE
	Raw Influent	Primary Effluent	Final Effluent	Sludge Disposed	
Full scale					
Chicago, U.S.A.				2290*	Patterson et al., 1975
Chicago, U.S.A.	0-9.5				Gurnham et al., 1979
Connecticut, New Jersey & New York, U.S.A.	0.02-0.84		<0.02-0.92		Mytelka et al., 1973
Dallas, U.S.A.	0-1.87				Weeks, 1975
Hawaii, U.S.A.	0.20-0.32	0.18-0.51	0.08-0.22	24-52	Nomura and Young, 1974
Indiana, U.S.A.	(2.07)		(0.233)	(13600)	Yost et al., 1981
Indiana, Michigan & Ohio, U.S.A.	0.1-3.0	0.3-2.7	0.1-1.2	73-232	U.S.P.H.S., 1965
Los Angeles, U.S.A.		0.430	0.104	3100*	Chen et al., 1974
Michigan, U.S.A.				1120-26,400*	Page, 1974
Muncie, U.S.A.	(0.79)-(1.15)		(0.24)-(0.27)		Davis and Jacknow, 1975
Nebraska, U.S.A.	(0.353)		(0.182)		Brown et al., 1973
New York, U.S.A.	0.27-0.80		0.16-0.49	51-161*	Klein et al., 1974
Ohio, U.S.A.	1.08-2.65	0.64-2.88	0.0-0.44	2335-11,000	Tarvin, 1956
Ohio, U.S.A.	0.42-0.48	0.25-0.30	0.05		Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	(0.648)	(0.527)	(0.229)		Davis and Jacknow, 1975
Wisconsin, U.S.A.				1930-12,100*	Cunningham et al., 1975
Calgary, Canada	0.075-0.240		0.022-0.105		McIntosh, 1980a
Calgary, Canada	0.075-0.238		0.037-0.072		McIntosh, 1980b
Edmonton, Canada				1200*	Dudas and Pawluk, 1975
Edmonton, Canada	(0.41)	(0.62)	(0.19)		Brown, 1979a
Edmonton, Canada	(0.15)	(0.43)	(0.11)		Brown, 1979b
Edmonton, Canada	0.07-0.75		0.028-0.100	6.78-18.70	Brown, 1980
Ontario, Canada	0-3.0	0-4.8	0-3.9	2.3-349	Abbott, 1971
Ontario, Canada				1100-9400*	Van Loon and Lichwa, 1973
Ontario, Canada	0.23-25.99	0.23-8.94	0.16-2.41	487-3050*	Oliver and Cosgrove, 1974
Ontario, Canada	0.11-2.40	0.07-1.13	0.04-0.56	310-24,000*	Oliver and Cosgrove, 1975
Ontario, Canada	0.04-8.1		0.03-2.6	1.2-520	Atkins and Hawley, 1978
Winnipeg, Canada	(0.565)			2500*	Carroll and Lee, 1977
60 plants, Germany			0.040-2.18		Mathys, 1979
Zurich, Switzerland	(0.6)		(0.25)	(3000)*	Roberts et al., 1977
Salford, U.K.	0.70-1.24				Stones, 1959b
Oxford, U.K.	1.2-2.3	0.31-0.60	0.06-0.13		Stoveland et al., 1979a

( ) arithmetic mean

plants and at various stages in these systems. This approach has been used to investigate the effects of various operating parameters, such as sludge age, on metals removal. Although this may be regarded as a functional approach, it does not provide rational predictive potential because it gives no quantitative information about phase distribution mechanisms and metal affinities.

2. A smaller second category involves studies in which more specific metal speciation measurements have been made in order to provide rational predictive information about metals removal.

2.1.4.1 Non-predictive Approach

Table 2.8 summarizes mean metal removal efficiencies measured in municipal activated sludge treatment plants.

The large variations in mean removal efficiencies for any one metal at a given plant and also among different sewage treatment plants are caused by varying conditions at and among individual plants. Factors affecting metals removal will be discussed in Section 2.2.

Although high overall removal efficiencies have been measured at different treatment plants for most of the metals, it appears that chromium, copper, lead and zinc are removed most efficiently and that nickel normally has the lowest removal efficiency. Removal efficiencies for nickel are usually less than 50% whereas those for the other metals are at least 60 to 70%. These data for nickel are consistent

TABLE 2.8 Average Metal Removal Efficiencies in Municipal Activated Sludge Treatment Plants (continued)

TYPE/LOCATION	% REMOVAL EFFICIENCY														REFERENCE
	PRIMARY TREATMENT							OVERALL TREATMENT							
	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Cd	Cr	Cu	Pb	Hg	Ni	Zn	
Pilot/Laboratory scale															
										60					McDermott et al., 1963a
						4	12			78			33	89	McDermott et al., 1963a, 1963b, 1965
									37	54			31	90	Barth et al., 1964
		6	10						44						Barth et al., 1965
									64-95						Bailey et al., 1970
									67	93			33	94	Wheatland, et al., 1971
												55*			Ghosh and Zugger, 1973
								38	57	33	56	69	21	65	Esmond and Petrasek, 1974
								32-77*				93*		8-55*	Neufeld and Hermann, 1975
										87*	98*		58*		Cheng et al., 1975
								47	19	14	45		18	31	Stoveland and Lester, 1980
								40-62							Weber and Sherrard, 1980

TABLE 2.8 Average Metal Removal Efficiencies in Municipal Activated Sludge Treatment Plants (concluded)

TYPE/LOCATION	% REMOVAL EFFICIENCY														REFERENCE
	PRIMARY TREATMENT							OVERALL TREATMENT							
	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Cd	Cr	Cu	Pb	Hg	Ni	Zn	
Full scale															
Chicago, U.S.A.								46		67	55		46	89	Patterson et al., 1975
Chicago, U.S.A.								>83							Lue-Hing et al., 1978
Connecticut, New Jersey & New York, U.S.A.										50	31			50	Mytelka et al., 1973
Hawaii, U.S.A.	29	26	50	48	67	14	51	59	32	74	73	95	42	71	Nomura and Young, 1974
Indiana, U.S.A.								81	98	85	95		29	89	Yost et al., 1981
Los Angeles, U.S.A.								64*	80*	69*	63*	76*	25*	75*	Chen et al., 1974
Muncie, U.S.A.									>78	>68	>71		<36	>70	Davis and Jacknow, 1975
Nebraska, U.S.A.								11	78	61	43	17		48	Brown et al., 1973
New York, U.S.A.								38	48	45			17	36	Klein et al., 1974
Ohio, U.S.A.		29	39			12	28		69	51			38	84	Turvin, 1956
Ohio, U.S.A.	50	0	0	32		25	38	75	46	50	25		18	90	Dugan and Pickrum, 1972
Pittsburgh, U.S.A.	14	17	23	54		1	19	67	67	56	82		10	65	Davis and Jacknow, 1975
Calgary, Canada									71	84	71		17	51	McIntosh, 1980a
Calgary, Canada								80	66	81	83		25	55	McIntosh, 1980b
Edmonton, Canada		10	32	8					57	54	16	26		54	Brown, 1979a
Edmonton, Canada		61	45						82	65		7		27	Brown, 1979b
Edmonton, Canada									91	77			2	81	Brown, 1980
Ontario, Canada	7	41	28	11		49	7	50	88	56	56		71	58	Abbott, 1971
Ontario, Canada	60	55	33	66	60	15	54	80	79	73	93	>85	16	77	Oliver and Cosgrove, 1974, 1975
Ontario, Canada								28	76	80	70	74	53	67	Atkins and Hawley, 1978
Winnipeg, Canada									83	75	78		28	56	Carroll and Lee, 1977
Zurich, Switzerland	30	40	40	50		35	35	35	70	55	65		45	60	Roberts et al., 1977
Salford, U.K.		28	45	40		21	41		70*	80*	90*		30*	57*	Stones, 1955, 1958, 1959a, 1959b, 1960
Oxford, U.K.	43		60	67				71		79	83				Lewin and Rowell, 1973
Oxford, U.K.	72	51	70	73		23	74	89	67	96	92		70	93	Lester et al., 1979a; Stoveland et al., 1979a

* removal due only to secondary treatment

with data from a recent U.S. report (Feiler, 1980), which showed that the median nickel removal efficiency in 20 sewage treatment plants was only 32%. The results for cadmium and mercury show the largest variations which may reflect the larger random analytical and sampling errors associated with the low concentrations of these metals generally found in municipal sewage.

In general, metal removal studies have used an operational definition of solubility based on the fraction of total metal which passes through 0.45 µm membrane filters. Raw sewage and final effluent data from laboratory scale activated sludge units have shown that chromium (at influent concentrations greater than 50 mg/L) was present predominantly in the soluble form whereas at lower influent concentrations (5 mg/L) it was mainly associated with particulate matter (Moore *et al*., 1961). Presumably the capacity of particulates to sorb chromium was exceeded at the higher concentrations. Irrespective of concentration used, nickel was predominantly soluble, copper was at least 50% soluble and zinc was mainly associated with particulates (Barth *et al*., 1965; Patterson *et al*., 1975). However, Mather (1964) reported that zinc in the effluent from a pilot activated sludge plant receiving high industrial zinc loadings was predominantly soluble. Rossin *et al*. (1982) found that the cadmium, copper and nickel in the effluent from a pilot plant receiving municipal primary effluent was largely soluble whereas chromium, lead and zinc were associated with poorly settleable particulates.

Heukelekian and Balmat (1959) have reported that 72%, 62.5% and 24% of copper, lead and zinc, respectively, in domestic sewage were associated with the settleable fraction. At the Bryan activated sludge plant in Ohio, chromium in the final effluent was predominantly soluble following a massive (500 mg/L) slug of chromic acid (English *et al.*, 1965). Almost all of the copper, nickel and zinc in the final effluent from a full scale plant in Ontario was in the soluble form (Oliver and Cosgrove, 1974). Results from a Los Angeles activated sludge plant showed that most of the lead and nickel in the primary effluent was soluble (< 8 μm diameter) while cadmium, chromium, copper and zinc were mainly insoluble (≥ 8 μm diameter). In the secondary effluent, more than 60% of each of the metals was soluble (Chen *et al.*, 1974). Nickel, chromium, copper and lead in the final effluent from an activated sludge plant in Hawaii were mostly soluble whereas cadmium and zinc were present predominantly in the insoluble phase (Nomura and Young, 1974). A recent size fractionation study using ultrafiltration in England found that most of the cadmium (45%) and copper (47%) in secondary effluent were associated with particles smaller than 0.015 μm in diameter whereas lead and some of the copper (32%) were associated with the largest size fraction (> 12 μM) (Laxen and Harrison, 1981).

It has been suggested that metal removal efficiencies are higher in secondary treatment plants than in primary plants mainly because suspended solids removal efficiencies are greater in the former (Brown *et al.*, 1973). More recent observations that proportions of dissolved/total metal concentrations increase as they pass through treatment plants (Chen *et al.*, 1974; Oliver and Cosgrove, 1974; Rossin *et al.*, 1982) support this suggestion.

Significant proportions of each metal are usually removed by primary sedimentation. This unit process appears to remove more copper, lead and zinc than the other metals. The higher removal efficiencies at the primary sedimentation stage observed in Great Britain can be partly explained by the long retention times (up to 12 h) used in the primary sedimentation tanks (Lester *et al.*, 1979a; Lewin and Rowell, 1973).

2.1.4.2 Predictive Models

There appears to have been two major attempts to quantitatively predict metal removal by biological treatment. A toxicity study is also included in this discussion because it demonstrates the importance of free metal ion concentrations. In presenting these studies, some of the symbols used have been changed to avoid confusion.

1. Major contributions to the modelling of metal removal in activated sludge systems have been provided by Dr. J. Patterson's research group at the Department of Environmental Engineering, Illinois Institute of Technology, IIT (Beers, 1979; Cheng *et al.* 1975; Hickey, 1979). These

investigators used the Schubert ion exchange method (Schubert, 1948; Schubert and Lindenbaum, 1952; Schubert *et al.*, 1950) in batch mode to measure conditional metal stability constants in wastewaters. This method is intended for use with trace concentrations of metals in the presence of a large excess of metal-complexing ligands and necessitates "swamping" standard and sample solutions with excess electrolyte.

Consider the following reactions of a metal ion, M, with wastewater ligand, L, and ~~cation~~ exchange resin (in the sodium form), RNa. Charges are omitted for simplicity.

$$M + nL \overset{K_L'}{\rightleftharpoons} ML_n \tag{2.1}$$

$$M + nRNa \rightleftharpoons R_nM + nNa \tag{2.2}$$

Metal distribution coefficients between the exchanger and the sample in the absence (λ_o) and presence (λ) of complexing agents are:

$$\lambda_o = \frac{[R_nM]}{[M]} \tag{2.3}$$

$$\lambda = \frac{[R_nM]}{[M] + [ML_n]} \tag{2.4}$$

Combining equations 2.3 and 2.4 with the equilibrium constant expression for equation 2.1 gives the following expression for determining the conditional stability constant, K'_L:

$$\log\left(\frac{\lambda_o}{\lambda} - 1\right) = \log K'_L + n\log[L] \qquad 2.5$$

Hence a plot of $\log(\frac{\lambda_o}{\lambda} - 1)$ versus $\log[L]$ under conditions such that $[L] \gg [M]$ will give a linear plot with slope equal to n and intercept equal to $\log K'_L$.

An expression for the conditional stability constant of metals with sludge, K'_s, was also developed based on the following reaction between metal ion, M, and y sorption sites on the sludge, S:

$$M + yS \xrightleftharpoons{K'_s} MS_y \qquad 2.6$$

The expression used to determine K'_s was:

$$\log \frac{[MS_y]}{[M] + [ML_n]} = \log K'_s - \log(1 + K'_L[L]^n) + y\log[S] \qquad 2.7$$

K'_L and n were evaluated according to equation 2.5, and K'_s and y were determined from a plot of $\log \frac{[MS_y]}{[M] + [ML_n]}$ versus $\log[S]$ keeping [L] and pH constant.

These measurements were made in raw sewage and primary effluents and combined with primary and secondary clarifier metal removal efficiencies and mass balance expressions to predict metal concentrations in primary and secondary effluents and in the sludges. Model simulations were made but no comparisons of predicted and measured removals were presented.

This work is important because it relates metal uptake by activated sludge to metal speciation in wastewaters and on the sludge. However, measurement of metal stability constants in media as complex and ill-defined as municipal sewage and sludge has the following limitations.

(i) The measured stability constants in ligand mixtures are not thermodynamic constants but are the sum of the individual conditional constants weighted by the respective mole fraction of each ligand present (Crosser and Allen, 1978). MacCarthy (1977) calls this the average stability constant. Inspection of equations 2.5 and 2.7 shows that stability constants can only be determined for known values of the ligand numbers, n and y, i.e. when the complexation reactions are well known. This is not the case for sewage or sludge. Metal complexes with one or two ligands per metal atom (i.e. ML and ML_2) have been suggested as occurring in natural water and soil systems containing humic and fulvic materials (Mantoura and Riley, 1975; Stevenson, 1977; Tan *et al.*, 1971). Furthermore, the method is not valid for polynuclear complexes, which contain more than one metal atom per molecule of complex. Gardiner (1974) found that humic acid molecules can complex more than one cadmium ion which is consistent with a polymeric ligand structure and perhaps with polymerization of the complex.

(ii) Equation 2.5 is valid only in terms of integral values of the ligand number, n (MacCarthy and Mark, 1977).

Integral values of n will be obtained for solutions of one or several ML complexes when all complexes have the same stoichiometry. For mixtures of complexes with more than one type of stoichiometry, integral values of n will be obtained only if one of the complexes is dominant (Crosser, 1975). The IIT group has found values of n and y to approximate integer values to within ± 30%, a variation which was attributed to analytical error.

(iii) The numerical value of stability constants depends on the ligand concentration units used (refer equation 2.5). The concentrations of complexing ligands in the earlier work (Cheng *et al.*, 1975) were measured in terms of chemical oxygen demand, COD, and total organic carbon, TOC, (for L) and volatile suspended solids (for S). Units for these measurements were mg/L, whereas the expressions developed require the use of molar units in order to allow comparison of stability constants. In the latter work (Beers, 1979; Hickey, 1979), ligand concentrations in sewage samples were converted to molar units by multiplying the TOC of the sewage by a value called the complexation capacity. This value was obtained by titrating sewage with metal and was defined as the moles of metal complexing capacity per unit (mg) TOC. No attempt at defining or measuring S in molar units was made.

2. In a second effort to quantify the metal removal process, Nelson *et al.* (1981) also measured stability constants and derived an expression which had the same form

as the Langmuir equation. They represented the reaction of soluble metal (free metal as well as all complexed metal forms), M', with unoccupied bacterial surface sites, S, as:

$$M' + S \overset{K'_A}{\rightleftharpoons} M'S \tag{2.8}$$

The equilibrium constant, K'_A, was given as:

$$K'_A = \frac{[M'S]}{C_{M'} \cdot \{S\}} \tag{2.9}$$

where $C_{M'}$ and [ ] denote concentration in moles/L, and { } is in g/L.

The total concentration of bacterial surface, $\{S_T\}$, was equal to the sum of unoccupied sites, S, and occupied sites, M'S, i.e.:

$$\{S_T\} = \{S\} + \frac{[M'S]}{y} \tag{2.10}$$

where y is the number of surface sites per unit mass of bacteria (moles/g).

Equations 2.8 to 2.10 were combined to give the following equation:

$$\frac{[M'S]}{\{S_T\}} = \frac{yC_{M'}}{y/K'_A + C_{M'}} \tag{2.11}$$

Equation 2.11 was simplified to give the expression for the linear part of the isotherm where $[M'] \ll y/K'$:

$$\frac{[M'S]}{\{S_T\}} = C_{M'} \cdot K'_A \qquad 2.12$$

This expression was used to quantify the relative affinity of activated sludge for cadmium, copper and zinc. No predictive or simulation studies were undertaken.

This method suffers from the same limitations as discussed for the work carried out at IIT. In addition, it does not allow determination of the ligand number but assumes a M/L ratio of 1/1 in the metal-ligand complexes.

3. The final approach was a toxicity study in which it was found that there was a positive correlation between copper/activated sludge ratios and free copper concentrations as determined by a copper ion selective electrode at constant pH (Braam and Klapwijk, 1981). The nitrification rate was also found to be inversely correlated to free copper concentrations but not to total copper concentrations.

2.2 FACTORS AFFECTING METAL REMOVAL

2.2.1 Physico-Chemical Factors

The metal species which are present in activated sludge depend on the species discharged and the reactions undergone by metals in the sewerage system and in the treatment plant. Metals in solution can exist in two broad categories (Stumm and Brauner, 1975). They can occur in the insoluble phase as precipitates and as ions attached to particulate matter; or in the soluble phase as free hydrated ions, inorganic ion pairs and as inorganic and organic complexes.

2.2.1.1 Physical State of Metals

It is obvious that metals associated with settleable particulate matter should be predominantly removed by primary sedimentation whereas removal of metals in other states will take place in the secondary aeration tank. Lead, for example, appears to be mainly associated with settleable suspended solids, whereas the poor removal of nickel in municipal treatment plants results from a combination of its highly soluble nature and its poor affinity for activated sludge.

2.2.1.2 Differences between Soluble Metals

There are essentially two broad aspects which have to be considered with respect to the different extents of uptake by activated sludge observed for different soluble metals.

1. Nieboer and Richardson (1980) have suggested a thermodynamic classification based on the relative proportions of Class A or Class B character that a metal exhibits. This can be represented as follows for the divalent metals.

$$Ca^{2+} > Mg^{2+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Hg^{2+}$$

Class A　　　　Borderline　　　　Class B

Class A metals have the following affinity sequence for metal-binding donor atoms in ligands:

$$O > N > S$$

In contrast, Class B metals exhibit the opposite preferences for these ligands.

Stumm and Brauner (1975) also state that whereas calcium and magnesium interact with anions by electrostatic interactions, complexes of the other metals also involve covalent forces which can be more important than electrostatic forces.

2. Frausto da Silva and Williams (1976) claim that the amount of metal taken up is proportional to the uptake factor, which is defined as:

$$\text{Uptake factor} = [M].\log K_A' \qquad 2.13$$

where [M] is the cation concentration and K_A' is the equilibrium constant for the uptake reaction. There do not appear to be large differences in log K_A' values between many of the divalent metals for complexation reactions with any carboxylic or dicarboxylic acid (Frausto da Silva and Williams, 1976). Hence selectivity of uptake is often based on relative metal concentrations.

The affinity of activated sludge for the metals, apart from nickel, appears to be much greater than that of competing organics in municipal sewage. This preference of metals for activated sludge occurs largely because of the much higher concentrations of complexing ligands on the sludge floc (Beers, 1979; Cheng *et al.*, 1975; Hickey, 1979; Patterson *et al.*, 1975). Many researchers have found the relative affinity of activated sludge for metals to be (Beers, 1979; Cheng *et al.*, 1975; Duggan and Pickrum, 1972; Guy, 1976; Hickey, 1979; Neufeld and Hermann, 1975):

$$Pb \geq Cu > Cd \geq Zn > Ni$$

Nelson *et al.* (1981) found that activated sludge had a larger affinity for zinc than for copper or cadmium. Chromium does not apear to form strong bonds with sludge (Mathys, 1979).

The relative affinities of activated sludge for the divalent metals being considered thus appear to closely follow the classificaton of Nieboer and Richardson (1980). This classification can also be used as an explanation for the high solubility of nickel compared to the other metals. Nickel is known not to readily form insoluble carbonate, hydroxide and phosphate complexes (Smith and Martell, 1976) and this is consistent with its low Class A character. It also forms stronger bonds with nitrogen and sulphur groups in sewage than with the oxygen groups which appear to be the dominant complexing sites on activated sludge.

Consideration of uptake factors can explain why uptake characteristics of metals can be greatly modified by the presence of larger concentrations of other metals, for example calcium. The growth inhibition of *E. coli* and *Lactobacillus sp.* by cadmium, nickel and zinc has been observed to be lowered markedly by the presence of up to 500 mg/L calcium, magnesium, manganese and strontium (Abelson and Aldous, 1950; MacLeod and Snell, 1950).

2.2.1.3 Metal Speciation in Wastewaters

Domestic wastewaters contain organic matter comprised of proteins (40 to 60% of total solids), carbohydrates (25 to 50%), fats and oils (10%). Typical concentrations of individual constituents in midwest U.S.A. domestic sewage are summarized in Table 2.9 (W.P.C.F., 1977). In addition, small quantities of "heavy metals" and a large number of synthetic organics of varying complexities are also present (W.P.C.F., 1977). Nitrilotriacetic acid, for example, has been used as a detergent builder in Canada since the late 1960's (Malaiyandi *et al.*, 1979). Fulvic and humic acids are naturally occurring ill-defined organic chelators which can undoubtedly also be present.

Information on specific metal compounds in municipal wastewaters is essentially non-existent. Atkins and Hawley (1978) have presented data which demonstrate the large number of inorganic and organic metal compounds which are used in domestic products and which can therefore potentially occur in municipal wastewaters. It is evident that wastewaters can contain halogen, nitrogen and sulphur complexing groups in addition to oxygen ligands.

There is a play-off between metal reactions in the wastewater and on the activated sludge because the two phases will compete for the soluble metals. The factors

Table 2.9 Typical Constituent Concentrations in Domestic Sewage (W.P.C.F., 1977)

Constituent	Concentration (mg/L)
Calcium	60
Magnesium	24
Sodium	80
Potassium	8
Phosphate	30
Sulphate	80
Silicate	26
Chloride	100
Bicarbonate	280
Ammonia nitrogen	30
Organic nitrogen	20

discussed in the previous section for metals uptake by activated sludge also determine metal speciation in wastewaters. Namely, the types and concentrations of the metals and ligands present and stability constants for the various metal complexation reactions are important. The total metal concentration does not affect metal complexation reactions when the ligand concentration is in excess as occurs in most environmental systems (Gardiner, 1974). As with metals uptake by activated sludge, these reactions can be expected to be quite rapid because they do not usually involve redox changes (Stumm and Brauner, 1975).

Speciation affects metal behavior in activated sludge systems. Copper sulphate has been observed to be sorbed to sludge to a much greater extent than copper cyanide (McDermott *et al*., 1963a). Funke (1975) also reported similar results for copper, but found that zinc cyanide was more efficiently removed than zinc sulphate. Metals have frequently been observed to be less effectively removed as concentrations of organic matter or of added complexing agents were increased (Adams *et al*., 1975; Beers, 1979; Gardiner, 1976; Hickey, 1979; Patterson and Minear, 1975; Patterson *et al*., 1975; Salotto *et al*., 1965; Stoveland *et al*., 1979a, 1979b, 1979c; Weeks, 1975). These data suggest that the ratio of uncomplexed to complexed metal is more relevant than total metal concentrations in considering treatment plant performances. Studies on natural waters support this view.

The presence of complexing agents in natural waters can reduce the concentrations of free metal ions (Gardiner, 1975; Stumm and Bilinski, 1973). Metal bioavailability and precipitation are thus reduced. Jenne and Luoma (1977) concluded that the thermodynamic activity of uncomplexed ions, and not total metal concentrations, could be the single most important factor affecting the biological uptake. Although further chemical reactions can generally only occur via the hydrated metal ion, it cannot be concluded that metal complexes are unreactive (Gardiner, 1975).

The relative tendency for complexation in natural waters and municipal sewage appears to be (Beers, 1979; Bender *et al.*, 1970; Chau and Lum-Shue-Chan, 1974; Gardiner, 1975; Helz *et al.*, 1975; Hickey, 1979; Lewin and Rowell, 1973; Stiff, 1971):

$$Cu > Cr > Ni > Cd > Zn$$

The above workers have reported proportions of cadmium, nickel and zinc present as the free metal ion to be 16 to 65% whereas less than 1% of chromium, copper and lead are normally present in the uncomplexed form. Complexation of cadmium, copper, nickel and zinc is believed to be primarily with organic ligands whereas chromium and lead form inorganic complexes most readily. Humic acids have been suggested as the major class of organic ligands in natural waters (Gardiner, 1974; Lewin and Rowell, 1973).

Another effect of complexation is to increase metal solubilities. Metal solubilities in ligand-containing samples are given by the sum of the concentrations of the free metal ion, soluble hydroxy species and of the various soluble metal complexes present (Stumm and Bilinski, 1973). Cadmium, copper, nickel and zinc are considerably more soluble in treated and untreated wastewaters than in tap or distilled water. Their solubilities in raw sewage have been calculated to be greater than could be accounted for by consideration of intrinsic carbonate, hydroxide and chloride metal salt solubilities (Patterson *et al.*, 1975). The solubilities of copper and nickel have been reported to be more strongly influenced by the concentration of soluble organic matter (as COD) than those of lead and zinc. Cadmium and chromium(VI) solubilities appeared to be independent of COD (Stoveland and Lester, 1980). Stoveland *et al.* (1979c) hypothesized that heavy metal loading to the activated sludge aeration tank can be increased as a result of metal complexation with, for instance, nitrilotriacetic acid, prior to secondary treatment. Continuous and shock loadings of sodium tripolyphosphate, on the other hand, resulted in decreased solubilities of cadmium, chromium, copper, lead, nickel and zinc (Stoveland *et al.*, 1979b, 1979c). The decreased solubilities were thought to be a consequence of the rapid hydrolysis of the tripolyphosphates to the relatively insoluble orthophosphates followed by their precipitation. Dugan and Pickrum (1972) also reported that metals removal by *Zoogloea* sp. was greatly enhanced when cells were washed by phosphate buffer because of the formation of insoluble metal phosphates.

The presence of synthetic complexing agents, such as the multidentate chelators ethylenediaminetetraacetic acid (EDTA) and NTA, can result in poor removal efficiencies of metals which are normally efficiently removed. Calculations have shown that EDTA, at concentrations which were found in sewage samples, would complex most of the trace metals to a significant extent (Gardiner, 1976). EDTA and NTA both form stronger complexes with metals than sludge or natural organics such as citrate, oxalate, amino acids, humic acids and tannic acids (Cheng *et al.*, 1975; Gardiner, 1976; Guy, 1976; Mathys, 1979). The affinity of EDTA for various metals decreases in the order (Laitinen and Harris, 1975; Mathys, 1979):

$$Hg > Cu > Ni > Pb > Zn > Cr \geq Cd$$

Snoeyink and Jenkins (1980) present the following stability order for metal-NTA complexes:

$$Cu > Pb > Ni > Zn$$

Warren (1974), however, found that NTA forms stronger complexes with cadmium, copper, mercury, nickel and zinc than with lead. These discrepancies cannot be explained without knowledge of experimental conditions such as pH and the presence of competing cations.

2.2.1.4 Oxidation State

Redox potentials range from -0.300 to +0.100 V for primary tank influents and from +0.10 to +0.540 V for activated sludge aeration tanks (Given, 1973; W.P.C.F., 1977). Inspection of standard electrode potentials (Cotton and Wilkinson, 1967; Laitinen and Harris, 1975) suggests that mercury can probably be present in raw sewage as the reduced elemental form, cadmium, nickel and zinc are probably present in the divalent oxidation states and chromium likely exists as chromium(III). Copper and lead may be able to exist in the elemental or divalent oxidation states depending on local conditions.

Elemental metal forms are probably removed by enmeshment in the sludge. Trivalent chromium, which in contrast to the other metals being considered does not undergo rapid complexation with organics (Cotton and Wilkinson, 1967), is readily hydrolysed to the insoluble oxide in neutral or mildly alkaline solutions such as municipal sewage (Bailey *et al.*, 1970; Cheremisinoff and Habib, 1972). Trivalent chromium is removed by activated sludge to a much greater extent than chromium(VI) (Ingols, 1954; Lamb and Tollefson, 1973; Stoveland and Lester, 1980).

Different valence states of the same metals may have different mechanisms of binding to sludge. Ogiwara and Kubota (1969) postulated that iron(II) combined with cellulose by forming weak ionic bonds with the carboxyl groups whereas iron(III) bonded by chelation.

2.2.1.5 Dissolved Oxygen Concentration

The oxidation state of metals is partially influenced by the dissolved oxygen concentration of the sewage. It is desirable to maintain activated sludge aeration tanks at minimum dissolved oxygen levels of 1 to 2 mg/L to prevent septic conditions (Metcalf and Eddy, 1979). Given (1973) stated that sewage becomes septic at redox potentials of 0 to -0.1 V.

Under anaerobic conditions, which can occur in "dead spots" of aeration tanks, cadmium, copper, lead, mercury, nickel and zinc can be precipitated as sulphides (Hao, 1978; Lawrence and McCarty, 1965). Hexavalent chromium is also readily reduced to chromium(III) by sulphydryl radicals (Ingols, 1954). Conversely, chromium(III) has been found to be oxidised only slowly to chromium(VI) by oxygen in natural waters (Schroeder and Lee, 1975). Insoluble influent metal salts such as copper sulphide have also been reported to be oxidised to soluble salts in aeration tanks (Barth, 1975).

Bacteria have been reported to be both able and unable to break down extracellular polymers under aerobic conditions (Obayashi and Gaudy, 1973; Wilkinson, 1958). Novak *et al*. (1977) observed that an anaerobic period of less than 24 hours caused polymer degradation. An aeration period of more than two or three hours was then required for the polymer content to increase. These results imply that metals can be released from sludge under anaerobic, and perhaps also under aerobic, conditions by bacterial degradation of extracellular polymers.

2.2.1.6 pH

The hydrogen ion activity strongly influences complexation, adsorption and precipitation reactions undergone by metals. These effects have been reviewed by Cheng (1973), Frausto da Silva and Williams (1976), Stumm and Bilinski (1973) and Van den Berg (1979).

Consider the following reaction:

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+ \qquad 2.14$$

where RO^- can be a binding site for metal cations.

pH can affect this reaction as follows:

1. Low pH values tend to reduce the degree of ligand dissociation, which consequently results in decreased adsorption and complexation. At a pH of 7, ligands such as carboxyl and phosphate will be favoured for cation uptake because they have pKa values which are considerably less than 7.

2. Protons can compete with metal cations at low pH values for binding sites in the sewage and on the floc. This affects conditional stability constants and occurs when the pH is smaller than one or more of the pKa values of complexing ligands.

3. When the pH is increased to a level at which other complexing anions can no longer successfully compete with the hydroxide ions present, metals will precipitate as

hydroxides.

A slight pH dependence of metal uptake either indicates that ligands are largely unprotonated in the pH range being studied or more likely that they are strong complexing agents which are relatively unaffected by pH changes (Gardiner, 1974).

Higher pH values can generally cause both increased metal uptake by activated sludge and increased metal solubilities due to increased complexation reactions in sewage, up to the pH value at which precipitation of metal hydroxides occurs (Beers, 1979; Gardiner, 1974; Hickey, 1979; Nelson *et al.*, 1981; Patterson *et al.*, 1975). It appears that changes in pH have a smaller effect on copper than on the other metals being considered. The optimum pH range for metal removal by activated sludge seems to be from 7 to 9, which encompasses the normal treatment operating pH range. Nelson *et al.* (1981) found that the maximum uptake of copper by activated sludge occurred near pH 7 whereas the uptakes for cadmium and zinc increased steadily from pH 6 to 9.

2.2.1.7 Temperature

The effect of temperature T, on acid dissociation constants, Ka, is given by the Van't Hoff equation (Cole and Coles, 1964).

$$\frac{d\ln Ka}{dT} = \frac{q}{RT^2} \qquad 2.15$$

where q is the heat absorbed per mole of reaction and R is the gas constant.

A temperature change from 0 to 50°C has very small effects on the dissociation constants of ammonia, acetic acid and phosphoric acid (Laitinen and Harris, 1975). Van den Berg (1979) calculated that large increases in temperature caused small decreases in both acid dissociation and stability constants for complexation of copper with glycine and NTA. He concluded, however, that these variations can partially or completely cancel each other when conditional stability constants are calculated.

It is also known that the effect of temperature on metal precipitation is complicated (Laitinen and Harris, 1975).

2.2.1.8 Ionic Strength

Increasing ionic strengths can potentially decrease the activities of ions, suppress the so-called double layer around large ionized organic molecules and colloidal particles and cause changes in ligand configurations.

The effect of ionic strength depends on the mechanism of cation uptake. It can be expected to have a considerably larger effect for ion exchange than for a complexation mechanism because in the former mechanism the background electrolyte will compete with the cation of interest for exchange with the cation exchanger. Ion-pair formation can also be a problem at high ionic strengths because of the decreased activity of metal ions. This effect, however, is probably unimportant in municipal sewage where the dissolved salt concentration is typically less than 0.01 M (W.P.C.F., 1977). The work of Schubert (1952) indicated that ionic strength only affected the activities of the individual metal and ligand ions.

Reductions in ionic strength to values approaching zero have been found to cause increases in concentration acid dissociation constants of organic ligands and the occurrence of mixed or polynuclear complexes and to decrease conditional stability constants of metal complexes (Coleman *et al*., 1956; Schnitzer and Hansen, 1970; Schubert, 1952; Stevenson, 1976, 1977).

2.2.1.9 Mixed Liquor Concentration

It is usually accepted that metal uptake by activated sludge increases with increasing mixed liquor solids (Cheng *et al*., 1975; Sterritt and Lester, 1981; Stoveland and Lester, 1980). Solids concentration in the aeration tanks can be controlled by varying the mean cell residence time, θd. Sterritt and Lester (1981) found that nickel removal, which was poor, was unaffected by θd and that optimum removal for the other metals occurred at θd values of 12 to 15 days.

2.2.1.10 Bacterial Physiological State

Bacterial extracellular polymer production increases as θd increases (Uloth and Mavinic, 1977). Increased removal efficiencies of metals can therefore be expected for older bacterial cultures (Friedman and Dugan, 1968; Nelson *et al*., 1981; Wilkinson, 1958). Nelson *et al*. (1981) found that copper uptake by activated sludge was only marginally affected by increasing θd values compared to cadmium and zinc. Furthermore, the concentration of soluble extracellular polymers decreases with increasing θd values (Saunders, 1975), so fewer competing metal complexation reactions may occur in the sewage itself.

It has also been reported that activated sludge grown under phosphorus-limited conditions adsorbed cadmium more readily than sludge grown under normal conditions. The reason given was that increased amounts of extracellular polymer were produced under nutrient-limiting conditions. This trend was, however, not observed for copper (Casey and Wu, 1978).

2.3 METHODS FOR METAL SPECIATION

The term "speciation" has sometimes been used to refer only to kinetically inert species present in aqueous samples. This type of speciation is accomplished by techniques such as filtration, solvent extraction, chromatography and some ion exchange methods. These techniques distinguish only between species that are not capable of rapid interconversion with one another; all interconverting kinetically labile species appear together as one "species". In other reports speciation is used in a broader sense to also differentiate between labile species. Methods used to determine labile species have included ion selective electrodes, ion exchange, voltammetry and anodic stripping. These methods must not perturb the positions of metal equilibria in the sample or must be able to correct for any perturbation caused by the analytical method. Six methods have been used for most metal speciation studies in environmental aqueous systems.

2.3.1 Calculation Method

Metals and ligands in natural waters participate in an interrelated network of chemical interactions (Stumm and Brauner, 1975). Calculation methods consequently require the simultaneous solution of appropriate mass action law and mass balance equations using pertinent total metal concentrations, concentrations of complexing ligands and stability constants of metal complexes. Computer models have been used to calculate equilibrium concentrations of metal species between aqueous and solid phases in the presence of inorganic and organic ligands (Florence and Batley, 1976; Morel and Morgan, 1972; Vuceta and Morgan, 1978).

This approach suffers from the following limitations (Florence and Batley, 1977; Gardiner, 1975).

1. Available knowledge on the nature and concentrations of naturally occurring metal-complexing ligands is often inadequate or unobtainable.

2. Relevant stability constant data are frequently not sufficiently precise or are not available.

3. Very little is known about metal-binding abilities of inorganic and organic colloidal particles.

4. It is frequently impossible to confirm computational results by direct measurement, particularly at low metal concentrations.

2.3.2 Size Separation Methods

Filtration through 0.45 µm membrane filters is frequently used to separate metals in the dissolved and particulate phases. This type of filtration, however, is based on an operational definition of solubility. Guy and Chakrabarti (1975) have presented data to show that free metal ions, humic substances and colloidal species can pass through 0.45 µm filters.

More information is obtained with the use of ultrafiltration and dialysis techniques. These physical separation methods have been widely used in natural water and wastewater studies (Benes and Steinnes, 1974, 1975; Chen *et al.*, 1974; Gjessing, 1970; Hoffmann *et al.*, 1981; Laxen and Harrison, 1981).

The following problems have been found with the use of filtration and dialysis methods.

1. Contamination may arise with filtration or dialysis media (Benes and Steinnes, 1974; Florence and Batley, 1977; Marvin *et al.*, 1970; Smith, 1976).

2. Filters may clog and leak (Demayo *et al.*, 1978; Hoffmann *et al.*, 1981).

3. Metal species may adsorb onto the large surface areas of the channels in filters and ultrafilters (Benes and Steinnes, 1974; Guy and Chakrabarti, 1975; Marvin *et al.*, 1970). Furthermore, Benes and Steinnes (1974) pointed out that adsorption may disturb metal-ligand equilibria because different forms of metals are usually adsorbed to different extents.

4. Equilibration times for the dialysis of cationic and neutral metal species are considerably faster than for anionic species, probably because the latter are repulsed by the negatively charged dialysis membranes (Benes and Steinnes, 1974). Neutral species and anionic species were found to equilibrate in two and seven days respectively. Guy and Chakrabarti (1975) found equilibration times of 24 and 60 hours for Cu-humic acid and $(Cu\text{-}EDTA)^{2-}$ respectively.

5. The assumption that free metal concentrations inside and outside dialysis bags are equal may not be correct and can lead to serious error (Guy and Chakrabarti, 1975).

Guy and Chakrabarti (1975) claimed that ultrafiltration is preferred to dialysis and anodic stripping voltammetry for metal speciation studies. It has, however, also been stated that size cutoffs in ultrafiltration are nominal and imprecise (Benes and Steinnes, 1974; Hoffmann *et al.*, 1981).

Gel chromatography has been used to study metal-organic ligand associations in sewage and sewage sludges (Baham *et al.*, 1978; Bender *et al.*, 1970; Rossin *et al.*, 1982; Tan *et al.*, 1971). These studies concluded that various metals are associated with particular molecular weight fractions, but did not generally give specific information regarding types of metal complexes and bonding.

Mantoura and Riley (1975) used gel chromatography to determine stability constants of copper, nickel and zinc complexes with humic acids. This is a dynamic equilibrium method to differentiate species which are kinetically inert or kinetically labile species for which the equilibrium positions are not finely balanced between the free metal ion and the complexes (Gardiner, 1975).

2.3.3 Solvent Extraction and Specific Chemical Methods

There appears to have been only limited application of solvent extraction for metal speciation studies in natural waters. Slowey *et al.* (1967) used chloroform extraction of seawater to separate ionic from non-ionic forms of copper, and Stiff (1971) used hexanol to separate copper associated with humic substances. Solvent extraction has been criticised for the following reasons (De Mayo *et al.*, 1978; Florence and Batley, 1977).

1. It probably provides incomplete extraction for organically-bound metal and for metal attached to organic colloidal particles.

2. Some of the metal on inorganic colloids may be extracted because these colloids tend to accumulate at the

organic-water interphase.

3. Solvent extraction results can vary with the concentration of suspended solids.

4. It is not known what forms of metals are extracted.

Chemical methods have often involved the formation of metal-chelate complexes and selectivity is achieved by pH control and by the use of masking agents. Stary (1964) has described the use of many chelating agents. The use of diphenylthiocarbazone (dithizone) and diethyldithiocarbamates appear to have been most widespread in studies of natural waters (Corcoran and Alexander, 1964; Foster and Morris, 1971; Fukai *et al.*, 1975; Williams, 1969). These studies have usually involved the formation of metal-chelate complexes before and after oxidation with perchloric acid, persulfate or ultra-violet digestion to assess the fraction of organically-bound metal. Other applications have been the use of neocuproine for copper speciation studies (Alexander and Corcoran, 1967; Stiff, 1971); and the use of 3-propyl-5-hydroxy-5-D-arabino-tetrahydroxybutyl-3-thiazolidine-2-thione (PHTTT) to determine copper bound by very stable "cyanide-like" ligands (Stiff, 1971).

Gardiner (1975) claims that at very low metal concentrations the extent of extraction using chelates can become non-quantitative. Furthermore, these methods can alter the position of metal equilibria in the natural samples. Kamp-Nielsen (1972) has calculated that copper complexes with stability constants less than 10^{30} will be decomposed by diethyldithiocarbamate and will be measured as ionic copper.

2.3.4 Voltammetry

The various polarographic methods can be used to determine about 20 metals which include cadmium, copper, lead, mercury, nickel and zinc (Peterson and Wong, 1981; Stumm and Brauner, 1975; Wang, 1982). Conventional polarography only gives reliable data at concentrations greater than about 10^{-5} $\underline{M}$ (Laitinen, 1975; Stumm and Brauner, 1975), which is higher than those normally measured in the environment. Sample concentration is not recommended because perturbation of metal equilibria may result (Ernst *et al.*, 1975). The use of pulse polarography, however, can increase detection limits by one or two orders of magnitude (Laitinen, 1975) and detection limits for anodic stripping voltammetry can be as low as 10^{-9} or 10^{-10} $\underline{M}$ (Peterson and Wong, 1981; Smith and Redmond, 1971; Stumm and Brauner, 1975). Anodic stripping has been found to be precise. Chau and Lum-Shue-Chan (1974) found relative standard deviations of 1.6 to 10% for the analysis of lakewater containing 5.0 to 24.5 p.p.b. of cadmium, copper, lead and zinc. Other features which have contributed to making anodic stripping voltammetry the most widely used analytical tool in metal speciation studies include its relatively modest cost, its simultaneous multi-element ability, the minimum sample pretreatment required, the small sample volume requirements and its ability to provide information on metal speciation (Blutstein and Smith, 1978; Peterson and Wong, 1981; Stumm and Brauner, 1975; Wang, 1982).

Anodic stripping voltammetry separates metal species on the basis of electrochemical "lability" rather than on the basis of stability constants (Allen *et al.*, 1976). Labile species are somewhat arbitrarily defined as those which dissociate at a rate greater than the reduction or plating rate (Lewin and Rowell, 1973).

Electroactive free metal and "labile" species (Guy and Chakrabarti, 1975) metal species have been measured in natural waters without sample digestion (Ariel and Eisner, 1963; Florence, 1972; Hoffmann *et al.*, 1981; O'Shea and Mancy, 1978; Smith and Redmond, 1971; Wang and Ariel, 1978). Anodic stripping voltammetry measurements made before and after sample digestion have differentiated between electroactive and "non-labile" or electroinactive (organic complexes plus colloidal species (Guy and Chakrabarti, 1975)) metal fractions in natural waters (Allen *et al.*, 1970; Batley and Florence, 1976; Blutstein and Smith, 1978; Chau and Lum-Shue-Chan, 1974; Laxen and Harrison, 1981) and in treated municipal sewage (Lewin and Rowell, 1973). Shuman and Michael (1978) used the rotating disc electrode with which the extent of reduction of "non-labile" complexes could be controlled by varying the rate of rotation of the electrode. They claimed to be able to differentiate between "labile" and "non-labile" complexes without the need for chemical digestion.

Differentiation between free metal ions and "labile" metal complexes can theoretically be made from shifts in peak positions towards more cathodic potentials (Stumm and Brauner, 1975; Wang, 1982) provided that the rate of complex formation is greater than the rate of oxidation or stripping from the electrode (Guy and Chakrabarti, 1975; Lewin and Rowell, 1973).

Anomalous anodic stripping results can be obtained for the following reasons.

1. The analytical procedure involves the addition of a supporting electrolyte such as acetate and lowering the sample pH to less than 5. Skogerboe *et al.* (1980) claim that these requirements may alter the types and concentrations of metal species from those originally present in the sample.

2. It is desirable when measuring free metal ions that metal complexes be non-reducible at the mercury electrode (Tuschull and Brezonik, 1981). The plating step lowers the metal concentration in the vicinity of the electrode and may consequently alter the overall position of metal-ligand equilibria with the result that the measured free metal ion concentration is too high (Hanck and Dillard, 1977; Shuman and Michael, 1978). Metal-carbonate and hydroxide complexes are electrochemically indistinguishable from free metal ions (Allen *et al.*, 1976), and metal-EDTA complexes are electrochemically labile (Hanck and Dillard, 1977; Shuman and Woodward, 1973; Tuschall and Brezonik, 1981). Free metal

ion concentrations can only be determined in the presence of these ligands if ligand concentrations as well as the pertinent ligand dissociation and metal formation constants are accurately known (Bhat *et al*., 1981; Hart, 1981; Shuman and Cromer, 1979).

3. Intermetallic compounds can be formed in the mercury of thin film mercury electrodes. Florence (1972) found that the stripping peak for zinc was depressed by the presence of copper and nickel in acetate buffer and that cadmium peaks were depressed by copper in citrate buffer. Formation of zinc-chromium, nickel-chromium and nickel-mercury intermetallic compounds has also been suspected (Smith and Redmond, 1971). This type of interference is rarely a problem with hanging mercury drop electrodes (Ariel and Eisner, 1963; Chau and Lum-Shue-Chan, 1974; Peterson and Wong, 1981).

4. Overlapping peaks may prevent reliable detection. Zinc and nickel have been observed to have the same peak current potentials with zinc masking the nickel which had a current sensitivity of only 7% compared to that of zinc. Copper, nickel and vanadium also appeared to have the same potentials (Smith and Redmond, 1971). These authors claimed that cadmium and lead were least affected and used the standard addition technique to overcome this problem. Ariel and Eisner (1963) used different supporting electrolytes to check for this type of interference.

5. Dissolved organic matter can become adsorbed onto the mercury surface causing changes in the reversibility of electrode reactions (Stumm and Brauner, 1975). Effects on voltammograms include depression of diffusion currents, wave shifts to more cathodic potentials and multiple waves (Schmid and Reilley, 1958). Ligands such as tannic acid, humic acid, gelatin and cysteine can have serious effects (Ernst *et al.*, 1975; Guy and Chakrabarti, 1975).

6. The reproducible condition of the electrode from one analysis to the next is imperative. This is a particular problem with thin layer mercury electrodes. Variations in the surface of these types of electrodes have been responsible for similar shifts in peak postions to those caused by complex formation (Gardiner, 1975; Hume and Carter, 1972). Hume and Carter (1972) also found the occasional appearance of uninterpretable double peaks.

Other interferences have been caused by cyanide (Chau and Lum-Shue-Chan, 1974) and by charged colloids which can interact with electrode surfaces (Blutstein and Smith, 1978; Brezonik *et al.*, 1976).

2.3.5 Ion Selective Electrodes

The use of ion selective electrodes has been popular because of their relatively low cost and because they are believed to respond only to free (uncomplexed) metal ions (Gardiner, 1975). Recently, however, it has been claimed that the copper electrode also responds to hydroxide and bicarbonate copper species in basic solutions (Wagemann, 1980). Measured cupric ion activities were found to be too high by factors of 10 and 40 at pH values 8.3 and 9.0 respectively.

A limitation of these electrodes is that they can only be used to determine the following few "heavy" metals: cadmium, copper, lead, mercury, silver and zinc (Orion Research, 1977). Furthermore, they generally do not show Nernstian response below 10^{-6} M (Blaedel and Dinwiddie, 1974; Gardiner, 1974; Stiff, 1971), which often causes them to be unsuitable for environmental studies. Jasinski *et al.* (1974), however, found linear Nernstian response for the copper electrode in seawater down to 10^{-8} M (0.0006 mg/L). Smith and Manahan (1973) used standard addition together with an acetate-fluoride complexing buffer to measure 5 x 10^{-8} M (0.003 mg/L) copper in natural water samples. Response times for steady state potentials to be obtained at environmental metal concentrations are typically at least ten minutes (Blaedel and Dinwiddie, 1974; Jasinski *et al.*, 1974; Florence and Batley, 1977).

The use of ion selective electrodes requires that sample measurements be compared to measurements made in standard solutions of the same constituents and ionic strength. The choice of electrolyte can alter the sensitivity. Stiff (1971) reported Nernstian response of the copper electrode down to 10^{-6} M and 10^{-8} M for solutions prepared in potassium nitrate and nitric acid (both at

5×10^{-3} M) respectively.

Ligands and some metals are known to shift equilibrium potentials to new values because of interaction in the membrane double layer region (Hansen *et al.*, 1972). Silver and EDTA, for example, have been found to interfere with copper electrodes (Blaedel and Dinwiddie, 1974; Jasinski *et al.*, 1974) and copper can contaminate cadmium electrodes (Gardiner, 1974). Bresnahan *et al.* (1978) and Buffle *et al.* (1977), however, found no evidence for adsorption of water and soil fulvic and humic acids onto electrode membranes. The equilibration of the electrode with the bulk solution causes metal from solution to be adsorbed onto the electrode surface. This adsorption lowers the metal concentration in solution and invalidates repeated measurements in samples containing low metal concentrations. Adsorbed metal on the electrode has also been found to affect electrode reponses (Blaedel and Dinwiddie, 1974).

2.3.6 Ion Exchange

Strong cation exchangers have been found to only partially remove trace metals from seawater. Even electrochemically labile metals were not completely removed, and with the exception of copper, bound metals were only removed to a small extent (Florence and Batley, 1976). Cation resins have been included in various chemical and size fractionation metal speciation schemes to differentiate metals which are very strongly complexed by soluble or colloidal ligands from other metal forms (Batley and Florence, 1976; Benes and Steinnes, 1975; Hart and Davies, 1979; Laxen and Harrison, 1981).

The use of the Schubert ion exchange method for the determination of stability constants has been discussed in Section 2.1.4.[illegible]. Although stability constant measurements require several assumptions that are tenuous when dealing with ill-defined samples, the use of the method to measure free metal concentrations (refer equation 2.3) can be made without any assumptions about the number and types of complexes formed. Furthermore, this method is independent of the units used to express ligand concentration (Crosser and Allen, 1978; MacCarthy and Mark, 1977). Beers (1979) and Hickey (1979) used equation 2.3 in their speciation studies of municipal sewage. Free metal ion and complexed metal concentrations in the parts per billion range were calculated. They did not, however, take account of the possible perturbation of metal-ligand equilibria which can occur when the Schubert method is used in the batch mode. Van den Berg and Kramer (1979) used very small amounts of a weak cation exchanger (manganese dioxide) in natural water studies in order to prevent perturbation.

Achilles *et al.* (1977) developed an equilibration batch-mode cation exchange method for the measurement of free magnesium in biological fluids. This method employed a low capacity ion exchange plug, used 1 mL sample volumes, and in contrast to the Schubert method, did not require the addition of excess electrolyte. Free magnesium concentrations were obtained from calibration curves of magnesium on resin versus free magnesium using standard solutions at the ionic strengths of samples being measured. A disadvantage of this method was the large influence of other cations, the concentrations of which were required to be accurately known. The extent of perturbation was calculated from a knowledge of total magnesium and ligand concentrations.

Batch ion exchange methods have been used to measure free calcium and magnesium in milk (Richardson *et al*., 1974; Van Kreveld and Van Minnen, 1955). This method also did not require addition of excess electrolyte. Perturbation of equilibria was prevented by equilibrating resin with milk after the same resin had been equilibrated with a standard solution containing the same concentration of potassium, sodium, calcium or magnesium as the milk sample. The small difference in calcium or magnesium on the resin between the standard and milk samples enabled free calcium and magnesium to be determined using simultaneous equations.

Flow through column or successive batch equilibration ion exchange methods have also been used in the dairy industry (Belec and Jenness, 1963; Christianson *et al*., 1954; Muldoon and Liska, 1969; Pearce and Creamer, 1974). These methods offer the advantage that the resin is brought to equilibrium with the unperturbed initial sample solution. However, because no excess electrolyte was added, these methods also rely on standard solutions containing the same concentrations of potassium, sodium, calcium or magnesium as the milk samples. Christianson *et al*. (1954) recognized that they did not know the sample ionic strengths exactly and consequently claimed to be measuring "apparent ion concentrations".

The methods described for use with biological fluids and milk are complex and not amenable to rapid routine use. Furthermore, they were not used under trace conditions: calcium and magnesium concentrations of 5 x 10^{-4} M to 2 x 10^{-3} M were measured.

Cation exchange methods exhibit some distinct advantages compared with other labile species-specific techniques such as ion selective electrodes or anodic stripping voltammetry.

1. They can be applied to the speciation of many different metals.

2. They are suitable at very low concentrations (e.g. 10^{-7} to 10^{-8} M, and much lower if radiotracers are used).

3. They are less subject to interference from other metals in solution.

4. They are free from adsorption interferences by organic matter (Allen *et al*., 1976).

They are, however, only strictly applicable to the study of uncharged or negatively charged complexes as positively charged complexes may be sorbed by the ion exchanger in addition to free metal ions.

2.3.7 Other Methods

The two oxidation states of chromium (Cr(III) and Cr(VI)) have been distinguished because Cr(III) is quantitatively co-precipitated on ferric hydroxide whereas the hexavalent state shows little tendency to co-precipitate (Chuecas and Riley, 1966; Jan and Young, 1978). Another method has used the selective chemiluminescence reaction with lophine which is undergone by Cr(VI) and not by Cr(III) (Marino and Ingle, 1981).

Indicator dyes have been used to determine free calcium and magnesium ion concentrations (Ashley and Campbell, 1979; Brinley *et al*., 1977; Fulton and Kratochvil, 1980; Tsien, 1980).

Various types of chromatography have been interfaced with specific metal detectors in the study of metal-organic ligand interactions. Atomic absorption spectrophotometers have been used with gas chromatography to study lead compounds (Chau *et al*., 1976; Coker, 1975; Segar, 1974) and mercury compounds (Gonzales and Ross, 1972; Longbottom, 1972) and with liquid chromatography in the study of copper compounds (Manahan and Jones, 1973). Direct current argon plasma emission (Uden *et al*., 1978) and atomic fluorescence (Van Loon *et al*., 1977) have also been used as detectors for chromatography.

2.4 MEASUREMENT OF METAL-COMPLEXING LIGANDS

The limited value of total organic carbon as a measure of organic compounds in natural waters has been recognized for some years (Cantillo and Segar, 1975). Only partial success has been achieved in the determination of specific organics for several reasons.

1. Separation procedures can exclude some metal-organic compounds.

2. The use of chromatography often involves detection with non-specific detectors.

3. Natural waters and wastewaters are of such complexity that it is highly unlikely that all metal-organics can be quantitatively determined.

Hence, methods for measuring metal-complexing ligands should not be specific for any one ligand unless it is known that it is predominantly responsible for the metal complexation and suitable analytical techniques are available for the ligand of interest.

The most widely used method for measuring so-called "metal complexation capacities" (Allen *et al.*, 1970) or "equivalent ligand concentrations" (Crosser and Allen, 1978) has been to titrate sample aliquots with the metal of interest. The response of the "probe" (e.g. ASV, cation exchanger, ion selective electrodes) to free metal ions is plotted as a function of total metal concentration or concentration of metal added. Metal titration curves have been discussed by Fulton and Kratochvil (1980), Lewin and

Rowell (1973) and Shuman and Woodward (1977). Addition of metal may displace other metals from their complexes or it may be taken up by non-metal containing ligands. The titration curve shows a sudden increase in slope and becomes linear when all the metal-complexing ligands have been consumed. The breakpoint represents the maximum concentration of metal that can be bound by ligands in the sample at the pH used, in other words, the metal complexing capacity.

Anodic stripping voltammetry, using peak currents, has undoubtedly been the most popular detection tool (Allen *et al.*, 1970; Bender *et al.*, 1970; Blutstein and Shaw, 1981; Chau and Wong, 1976; Chau *et al.*, 1974; Hanck and Dillard, 1977; Hart, 1981; Lewin and Rowell, 1973; Shuman and Woodward, 1977; Smith, 1976; Srna *et al.*, 1980). Copper has been commonly used because it generally forms more stable complexes than other methods for which voltammetry can be used (Shuman and Woodward, 1977). The limitations of anodic stripping voltammetry have been discussed in Section 2.3.4. Hart (1981) states that the titration curve measured by anodic stripping voltammetry will only have a distinct breakpoint if the product of the total ligand concentration and the overall conditional stability constant is considerably larger than one. Under natural water conditions this means that, for copper, only complexes with stability constants larger than 10^{10} will be measured (Chau and Wong, 1976; Hanck and Dillard, 1977).

Ion exchange equilibration methods have employed a weak cation exchanger (Van den Berg and Kramer, 1979) and strong cation exchangers (Beers, 1979; Crosser and Allen, 1977, 1978; Hickey, 1979; Zunino *et al.*, 1972). Crosser and Allen (1977) found that copper complexes of EDTA and glycine could be differentiated and that at a concentration of 4 x 10^{-4} $\underline{M}$, the minimum stability constant required for application of the method is approximately 2.5 x 10^3 L/mole. A non-equilibrium flow through method using Chelex 100 resin was claimed to have a detection limit of less than 5 x 10^{-8} $\underline{M}$ using EDTA as the ligand and copper as the titrant (Stolzberg and Rosin, 1977).

Other complexation capacity determinations have used ion selective electrodes (Bresnahan *et al.*, 1978; McCrady and Chapman, 1979; Sunda and Lewis, 1978); algal bioassays (Davey *et al.*, 1973; Gächter *et al.*, 1978; Srna *et al.*, 1980; Sunda and Lewis, 1978); a dialysis technique (Truitt and Weber, 1981); and, a method based on the increased solubilization of copper at pH 10 in the presence of complexing ligands (Kunkel and Manahan, 1973). These methods do not appear to have the sensitivity of anodic stripping or ion exchange methods and the solubilization method undoubtedly perturbs the natural equilibria present in the sample. However, of all the methods, free metal concentrations have only been measured directly using ion selective electrodes.

3. PROBLEM FORMULATION AND RESEARCH OBJECTIVES

Metals in municipal sewage can exist in the insoluble phase as precipitates and attached to particulate matter, or in the soluble phase in one or more forms. The form of the metal determines how and to what extent it is removed by activated sludge treatment systems. Metals in the particulate phase can be removed by primary sedimentation and by entrapment in the activated sludge. Soluble metals are removed by attachment to the activated sludge by one or more sorption processes. Activated sludge bacteria have been found capable of accumulating up to several percent of their weight as metal ions.

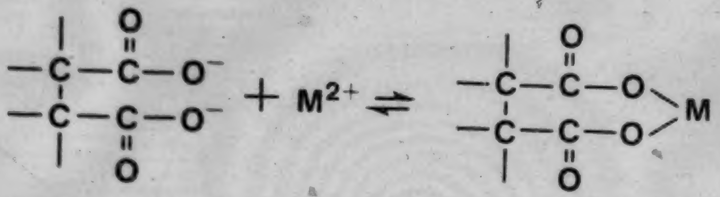
At least 90% of metals removal by activated sludge occurs rapidly (3 minutes to 3 hours) and uptake commonly follows Langmuir or Freundlich isotherms. Viability of the activated sludge appears to make little difference to this rapid uptake phase. Viable activated sludge may also show a subsequent second slow phase of metabolically enhanced active metal transport across cell walls and membranes.

It is evident that insoluble activated sludge extracellular polymers play an important role in metal uptake. These polymers appear to be predominantly polysaccharide in composition. Possible sorption mechanisms for soluble metals, M, onto activated sludge sorption sites, S, can be summarized into four categories.

1. Cation exchange.

$$2SNa + M^{2+} \rightleftharpoons S_2M + 2Na^{+} \qquad 3.1$$

2. Metal complexation with charged groups on the sludge. Although little is known about metal complexation with activated sludge, it appears that carboxyl and aliphatic hydroxyl groups are the predominant metal complexation sites. For example:



3.2

3. Metal complexation with uncharged ligands, L.

$$x(\text{Sludge-L}) + M^{2+} \rightleftharpoons (\text{Sludge-L})_x\text{-}M^{2+} \qquad 3.3$$

4. Adsorption of metal-organic molecules to parts of the sludge which do not contain ionized functional groups.

$$\text{Sludge} + \text{M-L} \rightleftharpoons \text{Sludge-M-L} \qquad 3.4$$

Only indirect evidence for the occurrence of the first two mechanisms has been presented in the literature.

Large variations in removal efficiencies within and among treatment plants occur for any of the metals. Removal efficiencies for cadmium, chromium, copper, lead, mercury and zinc are normally at least 60% to 70% whereas those for nickel are generally considerably less than 50%. Furthermore, the proportion of nickel removed by primary sedimentation appears to be less than for the other metals.

The relative affinity of activated sludge for metals appears to be:

$$Pb \geq Cu > Cd \geq Zn > Ni$$

Selectivity of uptake is based on metal character and on relative metal concentrations.

Information on specific metal compounds in municipal sewage is essentially non-existent, but the many and varied sources of metals and the complex nature of sewage suggest that the number of metal species can be large. Metal complexing ligands in wastewaters compete with those on the sludge for metals. Metal uptake by activated sludge undoubtedly occurs to a large extent because of the much higher concentrations of complexing ligands on the sludge than in the wastewater.

Metals have frequently been observed to be less effectively removed as concentrations of soluble organic matter or added complexing agents were increased. Reasons suggested for these observations have been that free metal ion concentrations were decreased and/or that metal solubilities were increased. The free metal ion has often been found to be the most important species governing metal behavior in many aqueous systems. Conversely, metal uptake increases when the concentration of biological solids in the aeration tank increases.

Metal uptake is also affected by high concentrations of other metals such as calcium and magnesium, oxidation state, redox potential, dissolved oxygen concentration, pH and mean cell residence times.

The prediction of metal removal in activated sludge treatment systems has concentrated on the measurement of conditional metal-ligand stability constants in wastewaters and with activated sludge. This practice requires several assumptions that are tenuous when dealing with ill-defined samples, not the least of which is related to the fact that the various ligands present are not known. Consequently, the numbers and types of metal complexes formed are not known. Furthermore, ligand concentrations have usually not been measured in molar units which means that the measured stability constants cannot be compared on a rational basis.

Anodic stripping voltammetry, ion-selective electrodes and ion exchange have been the most frequently used analytical techniques for metal speciation and complexation capacity studies. Of these methods, ion exchange exhibits distinct advantages in terms of applicability to many different metals, sensitivity and relative freedom from interference by other metals and organic matter. The Schubert ion exchange approach is considerably easier to use than other ion exchange methods which do not involve "swamping" samples with suitable electrolyte.

Only a few wastewater and sludge samples have been analyzed for metals at the City of Edmonton Gold Bar Wastewater Treatment Plant during the last five years. This lack of metals data in Edmonton necessitated the first research objective.

Inspection of equations 3.1 to 3.3 for uptake of soluble metals by activated sludge shows that the "active" metal species is the free metal ion. This suggests that the proportion of soluble metal present in sewage as the free metal ion might determine the extent of metal uptake. Although the free metal ion has often been implicated as determining metal behavior in other aqueous systems, particularly in toxicity studies, this species has not been explicitly evaluated for its role in metal removal by activated sludge. Hence, the other research objectives are based on the postulate that

> soluble metal uptake by activated sludge is primarily dependent on free metal ion (as opposed to total soluble metal) concentrations under equilibrium conditions.

Nickel is of concern because of its high toxicity and its poor removal by biological treatment. Quantitative speciation methodology for this metal is probably limited to anodic stripping and ion exchange. The current sensitivity of the former technique for nickel is, however, considerably less than for copper or zinc.

The research objectives were defined as follows:

1. To measure the influent concentration range and removal efficiency of nickel, relative to other metals of interest, at the Edmonton Gold Bar Wastewater Treatment Plant during dry weather flow conditions.

2. To develop a sensitive and accurate method for the measurement of free nickel ion concentrations in municipal sewage based on the Schubert cation exchange approach together with graphite furnace atomic absorption spectroscopy.
3. To use the developed ion exchange method to measure free nickel ion concentrations and nickel complexation capacities in Edmonton sewage.
4. To test the hypothesis that activated sludge uptake of nickel is a function of free nickel ion concentrations present at total nickel concentrations typical of municipal wastewaters.

4. EXPERIMENTAL

4.1 REAGENTS AND RESIN

High purity deionized water from a Millipore RO15-Q2 system was used throughout.

The analytical grade strong acid cation exchange resin was Dowex 50W-X8 (Baker Chemical Co., or Serva Corp.) of 50-100 mesh and with an exchange capacity of 4.9-5.2 meq/g of dry resin.

Hydrochloric acid, HCl (Amachem Co. or Fisher Scientific Co.), sodium hydroxide, NaOH (Amachem Co.), glycyl-L-alanine, gly-ala (Serva Corp.), disodium dihydrogen ethylenediaminetetraacetic acid dihydrate, $Na_2H_2EDTA.2H_2O$ (Baker Chemical Co.) and sodium nitrate, $NaNO_3$ (British Drug Houses) were either reagent or analytical grades. Aristar nitric acid, HNO_3 (British Drug Houses) and pesticide-grade methanol (Fisher Scientific Co.) were also used.

Certified Atomic Absorption Standard Solutions (Cd metal, $Cu(NO_3)_2$, $Ni(NO_3)_2$, ZnO in HNO_3 and potassium dichromate in water, Fisher Scientific Co.) were used to prepare all standard and synthetic solutions and for standard additions.

A reference quality control sample of dried municipal sludge from the U.S. Environmental Protection Agency (Spl.No.2792, WP976) was used for evaluation of wastewater digestion methods.

Medical grade carbon dioxide, CO_2 (Union Carbide Canada Ltd.) was used for pH buffering.

4.2 APPARATUS

An Instrumentation Specialties Company (ISCO) Model 1680 automatic wastewater sampler was used during the field study.

Metals were analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) using a Perkin-Elmer Model 5000 spectrophotometer with deuterium background correction, an HGA 2200 graphite furnace and an AS-1 auto sampling system with 20 µL injection volumes. Single element Perkin-Elmer Intensitron hollow cathode lamps and pyrolytically-coated graphite tubes were used.

Measurements of pH were made with a precision of ± 0.05 pH units using an Orion Ionalyzer 399A pH meter and an Orion Model 91-05 combination pH electrode calibrated with Orion pH standards of 4.0_0, 7.0_0 and 9.2_0 pH units.

Weighings were carried out on a Sartorius Model 1207 MP2 top-weighing balance (± 0.0001 g) and on a Mettler Model P1200 (± 0.002 g) top-weighing balance.

Samples were centrifuged in a Sorvall RC-5B refrigerated centrifuge (Du Pont Corp.) using SS-34 and GS-3 rotors, and in an IEC Model CL clinical centrifuge (International Equipment Co.).

Samples were shaken on a New Brunswick G-11 high speed gyratory shaker.

Vacuum filtrations were carried out using Whatman GF/C filters and 0.45 µm Millipore HAWP 04700 membrane filters together with Gelman plastic filter funnels with magnetic couplings (Gelman, Product No. 4200).

A Lab-Heat muffle furnace, Model M-30A-10 (Blue-M Electric Co.) was used for sample ashing.

Samples were digested using a Presto-brand aluminium pressure cooker and a Brinkman Model PT 10-35 homogenizer with a specially constructed titanium probe fashioned after the Brinkman PT 10 ST probe.

All glassware was constructed of borosilicate, and except for dispensing samples in suspended solids determinations, A-grade volumetric glassware was used. Wide tipped FisherBrand Serological pipettes (± 0.1 mL) were used to dispense samples onto filters for suspended solids determinations. Sewage samples were collected in 500 mL or 1000 mL Nalgene linear polyethylene bottles with screw caps.

Glass columns used in the determination of free nickel ion concentrations with the column ion exchange method consisted of a reservoir (8 cm long x 4.8 cm i.d.) fused to a long tubular section (26 cm long x 1 cm i.d.) which was in turn fused to a narrow section (0.5 cm i.d.) containing a Teflon stopcock. Plugs of glass wool above the stopcock were used to retain the resin. The volume of each column was about 100 mL (Figure 4.1).

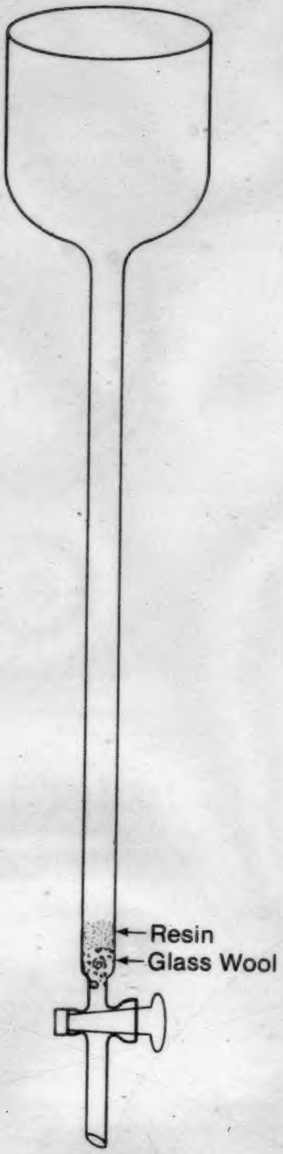

Resin
Glass Wool

Figure 4.1 Diagram of a Column Used for Ion Exchange Studies

Determinations for nitrilotriacetic acid, NTA, and total organic carbon, TOC, were carried out by technical staff in the Environmental Engineering Laboratory, University of Alberta. A single cell Princeton Applied Research Model 174A Polarographic Analyzer was used for NTA determinations. Total organic carbon analyses were carried out with a Beckman Model 915-B Tocamaster carbon analyzer.

4.3 PROCEDURES

4.3.1 Cleaning of Equipment

All laboratory and field equipment, including parts of the automatic sampler in contact with sample, were first cleaned by washing with detergent solution. After rinsing in tap water, they were soaked in 2 M HCl for several hours and rinsed thoroughly with high purity water. The glass columns together with the glass wool plugs were acid-washed by dripping about 600 mL of 2 M HCl through them followed by several washes with high purity water. Attempts to shorten the washing protocol led to the occurrence of spurious results.

4.3.2 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

Operating conditions for the spectrophotometer and furnace are listed in Table 4.1 for various matrices used in this study. The furnace temperature and time conditions were optimized by following Perkin-Elmer instructions (Perkin-Elmer, 1977) using standards and sewage samples. It was found necessary with the higher ionic strength matrices (i.e. sample matrices 2 and 3) to use uninterrupted gas flow (i.e. "Norm") to prevent condensation on the furnace windows. Either peak heights or areas were measured as appropriate for obtaining optimum absorbance values.

Zinc was determined using a wavelength of 307.8 nm rather than the more sensitive 213.9 nm because exceedingly high and variable blank absorbance values were obtained when the second wavelength was used.

Typical GFAAS calibration curves for standard cadmium, chromium, copper, nickel and zinc solutions prepared in 1% HNO_3 (by volume) and employing new or near-new graphite tubes are presented in Appendix A.

The linear absorbance ranges for these metals, obtained from the calibration curves, are summarized in Table 4.2. Where necessary, samples were diluted so that their absorbance values were within the linear range. Absorbance values for appropriate blanks were subtracted from standard and sample absorbances prior to calculation of concentrations. Blanks and standards were run after about every third sample to correct for furnace drift and deterioration of graphite tubes. Triplicate injections were used for all blank, standard and sewage samples. The mean absorbance value of two or three injections was used to

Table 4.1 Operating Conditions for the Atomic Absorption Spectrophotometer and Furnace

Conditions	Metal					
	Cd	Cr	Cu	Ni	Ni	Zn
Sample matrix(1)	a	a	a	a	b,c	a
Wavelength (nm)	228.8	357.9	324.7	232.0	232.0	307.6
Slit width (nm)	0.7Low	0.7Low	0.7Low	0.2Low	0.2Low	0.7Low
Integration time (s)	5.0	10.0	5.0	5.0	5.0	5.0
Gas flow (mL/min)	--	--	--	--	50	--
Flow time (s)	7(Stop)	7(Stop)	7(Stop)	7(Stop)	7(Norm)	7(Stop)
Drying temp. (°C)	85	85	85	85	85	85
Drying time (s)	40	40	40	40	40	40
Ashing temp. (°C)	300	1100	650	800	800	300
Ashing time (s)	35	35	40	35	35	35
Atomization temp. (°C)	2100	2700	2700	2700	2700	2400
Atomization time (s)	5.0	10.0	5.0	5.0	5.0	5.0
Measuring mode (Peak)	height	area	area	area	area	height

(1) Sample matrices are:
a. 1% HNO_3
b. (0.10 - 0.30 $\underline{M}$) $NaNO_3$ + 1% HNO_3
c. 2 $\underline{M}$ HNO_3

Table 4.2 Linear Absorbance Ranges for Metals Analyzed by GFAAS

Metal	Linear Range	
	M	(mg/L)
Cd	0 - 9.0×10^{-9}	0 - 0.0010
Cr	0 - 2.0×10^{-7}	0 - 0.010
Cu	0 - 4.0×10^{-7}	0 - 0.020
Ni	0 - 4.0×10^{-7}	0 - 0.020
Zn	0 - 8.0×10^{-5}	0 - 5.0

calculate each concentration. Absorbance values were only accepted if they were within 10% of each other for any one sample.

Replicate injections of low concentration standard metal solutions were carried out to estimate the accuracy and reproducibility of the GFAAS methods. Table 4.3 shows these results. All standard solutions were analyzed accurately and with good reproducibility. The largest relative standard deviation was 8% for chromium.

4.3.3 Interferences in GFAAS

One or more of the following categories of interferences can occur with the use of GFAAS (Krasowski and Copeland, 1979; Perkin-Elmer, 1977).

1. Background (molecular) absorption or scattering is caused when components of the matrix volatilize during sample atomization. It can be overcome by using background correction.

2. Spectral interference can occur when spectral lines overlap.

3. Chemical and physical interferences arise when the number of ground state metal atoms generated during atomization is reduced. An example of this is the formation of non-volatile metal-carbides by interaction of metals with the graphite tube. This type of interference always causes suppression of GFAAS signals.

Table 4.3 Results of Replicate Injections of Metal Standard Solutions

Parameter	Metal					
	Cd	Cr	Cu	Ni	Ni	Zn
Matrix(1)	a	a	a	a	b	a
Prepared standard concentration	8.90×10^{-9} (0.0010)(2)	9.62×10^{-8} (0.005)	3.15×10^{-7} (0.020)	1.70×10^{-7} (0.010)	3.40×10^{-7} (0.020)	7.65×10^{-6} (0.50)
n(3)	20	20	20	20	10	21
Mean	8.90×10^{-9}	9.71×10^{-8}	3.15×10^{-7}	1.70×10^{-7}	3.40×10^{-7}	7.69×10^{-6}
Standard deviation	$<4.4 \times 10^{-10}$	7.6×10^{-9}	1.0×10^{-8}	1.2×10^{-8}	1.5×10^{-8}	2.6×10^{-7}
Relative standard deviation (%)	<5	8	3	7	4	3

(1) Sample matrices are: a. 1% HNO_3
b. 0.10 M $NaNO_3$ + 1% HNO_3

(2) Parentheses represent concentrations in mg/L. Other concentrations are moles/L.

(3) Each result is the mean of two or three injections.

4. Matrix interferences occur when the rate of analyte atomization is changed and can give rise to either enhancement or suppression of measured signals. They commonly occur when the physical and chemical characteristics of standards and samples are considerably different. For example, covolatilization of metal along with a more volatile matrix can occur in natural samples. This effect can be overcome by the method of standard additions provided that the added metal behaves similarly to the metal present before standard addition.

The causes and mechanisms of chemical, physical and matrix interferences are not known in detail, but they appear to be related to the furnace construction and type of heating used. Rates of heating are relatively low, heating is non-isothermal in time and length along the length of the graphite tube (Chakrabarti *et al.*, 1980), the vapour temperature lags the wall temperature (Hageman *et al.*, 1979), the porosity and surface condition of graphite tubes is in a state of continual change (Willis, 1975) and residence times of atomized metals are short and can be variable (Hageman *et al.*, 1979) in commercial AAS graphite furnaces.

Pyrolytically-coated graphite tubes were used throughout this program to reduce the possibility of metal-carbide formation. The presence of matrix interferences in sewage samples was checked by the method of standard additions. Small volumes (< 1% of total volume) of concentrated metal standard solutions were added to undiluted and diluted sewage and mixed liquor samples acidified with 1% HNO_3 (by volume). The acidified samples were digested using the homogenization method (refer Section 4.3.5). Metal recoveries were compared with those for standard metal solutions prepared in the same manner. Unspiked sewage and 1% HNO_3 solutions were used as blanks. In view of the use of centrifugation to remove particulate material from wastewaters prior to analysis for free nickel (refer Section 7.2), the nickel studies were also carried out on uncentrifuged and centrifuged samples. Samples were diluted to determine whether interferences which might occur could be overcome by dilution.

Metal recoveries from the spiked samples are summarized in Table 4.4 together with the concentrations of the standard additions (spikes) used. The only cases of incomplete recovery occurred with the determinations of cadmium in mixed liquor diluted 1:25 and chromium in raw sewage diluted 1:10. Consequently, mixed liquor samples for cadmium analyses and unfiltered raw sewage samples for chromium analyses were always diluted ≥ 1:50 and 1:100 respectively before determinations were made for these metals. These dilutions were sufficient to ensure that absorbance values were within linear working ranges of the calibration curves. The results in Table 4.4 also demonstrate that accurate analyses were possible using standards prepared with 1% HNO_3 (by volume).

Table 4.4 Metal Recoveries from Spiked Sewage and Mixed Liquor Samples

Sample	Dilution	Treatment(1)	Metal Recovery (mg/L)				
			Cd	Cr	Cu	Ni	Zn
Spike(2)		None	0.0002	0.0025	0.010	0.010	0.025
Raw sewage	None	None				0.011	0.024
	None	a				0.009	
	None	b				0.009	
	None	c				0.010	
	1:2	None			0.011	0.010	
	1:5	None	0.0002		0.010	0.011	
	1:10	None	0.0002	0.0013	0.012	0.011	
	1:100	None	0.0002	0.0025	0.011		
Spike(3)		None	0.0004	0.0025	0.010	0.010	0.100
Mixed liquor	1:10	None					0.08
	1:25	None	0.0001		0.010	0.011	
	1:50	None	0.0004		0.009	0.011	
	1:100	None	0.0004	0.0026		0.009	
	1:1000	None		0.0023			

(1) Sample treatments:
a. Centrifugation at 5000 r.p.m. (12 075 x g) for 10 min.
b. Centrifugation at 9000 r.p.m. (13 000 x g) for 10 min.
c. Centrifugation at 20,000 r.p.m. (48 300 x g) for 10 min.

(2) Refers to final concentrations of metal standards added to raw sewage samples.

(3) Refers to final concentrations of metal standards added to mixed liquor samples.

4.3.4 Sample Preservation

Sewage samples not intended for the determination of free nickel were acidified with HNO_3. Nitric acid is the preferred mineral acid for GFAAS. Losses of volatile metal chlorides can occur with hydrochloric acid, sulphuric acid can form insoluble metal sulphates with, for example, lead (Carrondo *et al.*, 1979a, 1979b) and low metal recoveries have been experienced with the use of perchloric acid (Dokiya *et al.*, 1975). The use of varying amounts of concentrated HNO_3, up to 0.5% on a volume basis, has been recommended (APHA, 1975; Environ. Can., 1981), and EPA (1976) recommends the addition of sufficient HNO_3 to decrease the sample pH to less than 2 for the preservation of wastewater samples. The addition of 1% (by volume) of concentrated HNO_3 was used in this study in view of the acid requirements for the homogenization digestion method (refer Section 4.3.5).

Sample preservation, if required, was carried out immediately after collection, and analytical procedures on samples not requiring preservation were started within 1 h of collection. Unpreserved sewage samples requiring standard metal additions were left for at least 2 h after standard additions before starting the experimental procedure to allow the added metal to equilibrate with the metal-complexing ligands present.

4.3.5 Choice of Sample Digestion Method

Digestion of natural samples may be necessary before analysis of metal concentrations to destroy the organic matrix and to solubilize the metals. Dry ashing has been found to be less efficient for some metals than wet ashing techniques (Carrondo *et al.*, 1979b; Delfino and Enderson, 1978; Jenniss *et al.*, 1980). Hot HNO_3 digestion is recommended for wastewaters by at least two standard methods (APHA, 1975; EPA, 1976). Jenniss *et al.* (1980) found that hot HNO_3 digestion gave low results for metals in sludges and that the use of HNO_3 in a high pressure decomposition vessel or HNO_3 together with hydrogen peroxide gave the best metal recoveries. Digestion of acidified sludge in an autoclave at 15 psig for 2 h was used by Cheng (1973). The advantages of steam digestion under pressure are that it is simpler and faster for large numbers of samples compared with other digestion methods and it prevents volume loss by evaporation when compared to dry heating methods such as sand baths.

Digestions of municipal wastewaters and sludges have also been carried out using high speed homogenization with a specially constucted titanium probe instead of the stainless steel probe supplied in order to prevent metal contamination (Lester *et al.*, 1977). Acidified samples (1% by volume with HNO_3) were homogenized for 5 min at 8000 r.p.m. (Carrondo *et al.*, 1979a, 1979b; Stoveland *et al.*, 1978).

Digestion by this method is achieved by mechanical grinding and ultrasonic waves generated by the probe. These investigators reported that the homogenization method yielded results for a wide range of metals which were statistically similar to those using HNO_3/H_2SO_4, H_2O_2/HNO_3 or bomb digestion methods. The major advantage of digestion by homogenization was claimed to be its speed compared to standard wet acid digestion methods.

It was decided to compare acid digestion using steam under pressure (hereafter called pressure digestion) with the hot HNO_3 digestion method of APHA (1975) and high speed homogenization using a titanium probe. Nine aliquots were taken from bulk samples of uncentrifuged raw sewage, mixed liquor and primary sludge to allow each digestion method to be carried out in triplicate for each type of sample. Raw sewage samples were undiluted and the mixed liquor and sludge samples were diluted 1:10 with high purity water prior to digestion. The HNO_3 digestion method used 20.0_0 mL samples, the addition of 3 successive 35 mL aliquots of concentrated HNO_3 (Aristar) which were boiled to dryness and the final addition of 20.0_0 mL of 1% HNO_3 (by volume) to dissolve the residue. Samples for digestion by the other two methods were acidified (1% by volume) with HNO_3 before digestion and 20.0_0 mL aliquots were used. Homogenization was carried out for 5 min at near maximum speed (setting 8). Pressure digestion was carried out in Pyrex boiling tubes covered with acid-washed aluminium foil for 1 h at 15 psig in an aluminium pressure cooker. Blank samples (i.e. 1% HNO_3 by volume) were digested in the same manner as the sewage samples.

Table 4.5 shows the results of this comparative study. The pressure digestion method was at least as efficient for digestion of all but two of the samples used as the other two methods. Blank absorbance values for the pressure digestion method were negligible whereas those for cadmium, chromium and nickel using the HNO_3 digestion and homogenization methods were unacceptably high. The pressure digestion method was by far the easiest to carry out, whereas great care was necessary with the wet HNO_3 digestion method of APHA (1975), and the noise generated by the homogenizer was virtually unbearable even with ear protection.

The pressure digestion method was further evaluated by analyzing, in triplicate, a sample of reference municipal sludge from the U.S. Environmental Protection Agency. Table 4.6 demonstrates that this method gave results which agreed to within 2 standard deviations with those supplied for the reference sludge.

Pressure digestion was thus the preferred digestion method. Although some samples were initally digested using high-speed homogenization, most of the samples requiring digestion were acidified with HNO_3 and digested in a pressure cooker as described.

Table 4.5 Comparison of Digestion by Hot HNO_3, Homogenization and Pressure Digestion

	Digestion[(1)] Method	Metal Concentration (mg/L)[(2)] Cd	Cr	Cu	Ni	Zn
Raw sewage	a	0.0016±0.0003	0.243±0.008	0.069±0.010	0.031±0.000	0.30±0.03
	b	0.0025±0.0002	0.172±0.003	0.081±0.021	0.062±0.006	0.29±0.01
	c	0.0031±0.0004	0.245±0.009	0.090±0.011	0.052±0.003	0.31±0.01
Mixed liquor	a	0.0205±0.0030	2.00±0.00	0.433±0.194	0.213±0.029	2.3±0.2
	b	0.0183±0.0010	1.42±0.14	0.167±0.029	0.195±0.000	1.6±0.0
	c	0.0150±0.0000	2.00±0.00	0.375±0.025	0.217±0.028	1.4±0.2
Primary sludge	a	0.129±0.007	10.5±0.30	4.62±0.15	1.20±0.00	10±0.0
	b	0.099±0.000	10.4±0.17	4.18±0.11	1.40±0.03	10±0.0
	c	0.116±0.007	12.7±0.37	4.72±0.03	1.50±0.03	12±0.0

(1) Digestion methods: a. Hot HNO_3
b. Homogenization
c. Pressure digestion

(2) Concentrations presented as mean ± 1 standard deviation based on triplicate injections of three samples.

Table 4.6 Total Metal Concentrations for EPA Municipal Sludge Determined after Pressure Digestion

Metal	Measured Concentration(¹) (mg/kg)	Reference Concentration(¹) (mg/kg)
Cd	19.4 ± 4.2	20.8 ± 9.15
Cr	176 ± 6.0	204 ± 45
Cu	901 ± 31.5	1095 ± 132
Ni	205 ± 7.5	198 ± 17.5
Zn	1188 ± 54.5	1323 ± 65

(¹)Concentrations as mean ± 1 standard deviation

4.3.6 Determination of Solids, Total Organic Carbon and Nitrilotriacetic Acid

Total solids, mixed liquor suspended solids and volatile suspended solids were determined according to APHA (1975).

Determination of TOC used acidified samples (1% HNO_3 by volume) without sample neutralization before injection into the Beckman carbon analyzer.

Nitrilotriacetic acid was determined polarographically using the method of Environ. Can. (1979) except that a single rather than a double cell polarographic analyzer was used.

4.3.7 Resin Preparation

Fines were removed by repeated sedimentation and decantation in water. About 25 g of fines-free resin was transferred into a 2.5 cm i.d. glass column and washed with 4 M HCl until the effluent was colourless. The resin was then washed with water until the effluent and influent pH values were the same. Next it was converted to the sodium form by washing with 3 M NaOH until the pH of the effluent no longer increased. This was followed by a water wash until effluent and influent had the same pH values. The resin was finally washed with 250 mL methanol followed by a wash with water before being dried at 45°C in a convection oven and stored in a screw-cap polyethylene bottle.

4.3.8 Data Analysis

Data manipulations and statistical analyses were carried out with the University of Alberta Amdahl 470V/6 computer together with the MIDAS data handling and statistical package. Fortran programs calling the CGPL plotting subroutine were used for all computer graphics.

5. TOTAL METAL CONCENTRATIONS AND REMOVAL EFFICIENCIES AT THE EDMONTON GOLD BAR WASTEWATER TREATMENT PLANT

The municipal wastewater treatment plant in Edmonton, the Gold Bar Plant, is a plug-flow activated sludge plant. At the time of this study it had a design capacity of 495 ML/d for primary treatment and 205 ML/d for secondary treatment. Figure 5.1 shows the layout of the treatment process. Treated wastewaters are discharged to the North Saskatchewan River and digested sludge is pumped to the Clover Bar Sludge Storage Lagoons. The study was carried out during June 6 to June 14, 1980, a period when there was no rainfall and there was no flow of supernatant from the Clover Bar Lagoons. Daily plant operational performance data for this period, in terms of BOD_5 and suspended solids removal, are summarized in Table 5.1.

5.1 PROCEDURES

Discrete 75 mL samples were collected at 15 minute intervals using an automatic wastewater sampler located directly downstream from the right side bar screen (Site A, Figure 5.1). Four consecutive samples were automatically collected in each sample container to provide 1-hour composite samples for two 12-hour and three 24-hour periods. Manual grab samples were collected at 6-hour intervals from the other two bar screen outlets and at 12-hour intervals

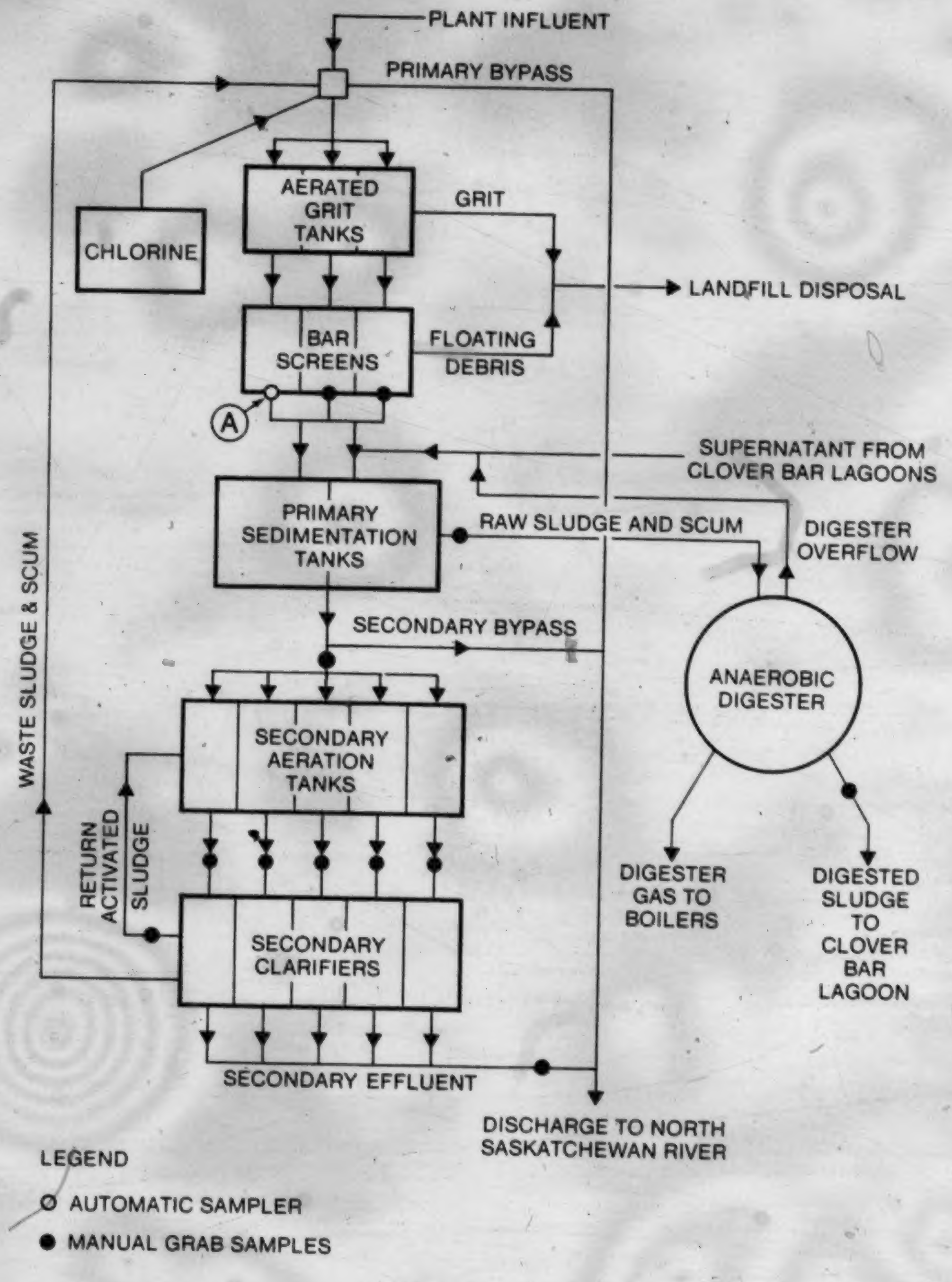

PLANT INFLUENT
PRIMARY BYPASS
AERATED GRIT TANKS
GRIT
CHLORINE
LANDFILL DISPOSAL
BAR SCREENS
FLOATING DEBRIS
A
SUPERNATANT FROM CLOVER BAR LAGOONS
PRIMARY SEDIMENTATION TANKS
RAW SLUDGE AND SCUM
DIGESTER OVERFLOW
SECONDARY BYPASS
ANAEROBIC DIGESTER
WASTE SLUDGE & SCUM
SECONDARY AERATION TANKS
RETURN ACTIVATED SLUDGE
DIGESTER GAS TO BOILERS
DIGESTED SLUDGE TO CLOVER BAR LAGOON
SECONDARY CLARIFIERS
SECONDARY EFFLUENT
DISCHARGE TO NORTH SASKATCHEWAN RIVER
LEGEND
○ AUTOMATIC SAMPLER
● MANUAL GRAB SAMPLES

Figure 5.1 Layout of the Gold Bar Wastewater Treatment Plant Showing Sampling Sites

Table 5.1 Daily Operational Performance (24 h composites) at the Gold Bar Wastewater Treatment Plant during the Study Period

Date	BOD_5			Suspended Solids		
	Influent (mg/L)	Final effluent (mg/L)	% removal efficiency	Influent (mg/L)	Final effluent (mg/L)	% removal efficiency
June 6	206	18	91	255	10	96
7	203	33	84	242	12	95
8	129	33	74	167	13	92
9	126	31	75	133	11	92
10	196	25	87	227	12	95
11	223	29	87	291	14	95
12	235	25	89	369	13	96
13	212	37	82	249	16	94
14	206	32	84	233	12	95

from the primary effluent, final effluent, mixed liquor, return sludge, primary sludge and digested sludge. All mixed liquor and return sludge samples were equal volume composites of samples collected from each of the five secondary aeration tanks. Primary and digested sludges were collected from the cones of the primary sedimentation tank and one of the sludge digesters respectively.

The wastewater samples were vacuum filtered through membrane and Whatman GF/C glass fibre filters, with the latter acting as prefilters. Sludge samples were diluted 1:10 (by volume) prior to addition of acid and all samples were digested in a pressure cooker before being analyzed for metals.

All samples were analyzed for cadmium, chromium, copper, nickel and zinc. Total solids analyses were used to convert units of mg/L in mixed liquor and sludge samples to mg/kg (dry weight).

Flow data were obtained from the Gold Bar Wastewater Treatment Plant records. Hourly loadings were calculated from the following expression:

$$\text{Loading(kg/h)} = \text{Flow(ML/h)} \times \text{Concentration(mg/L)} \quad 5.1$$

The concentration data for each of the metals were positively skewed. Data were consequently transformed to natural logarithms prior to statistical analysis (refer Section 5.2.2).

5.2 RESULTS AND DISCUSSION

All metal concentration and flow data are provided in Appendix B. Each concentration represents the mean of triplicate analyses.

5.2.1 Influent Metal Concentrations

Table 5.2 summarizes ranges and means of the total metal concentrations determined in influent samples to the Gold Bar Wastewater Treatment Plant together with data from other municipal treatment plants in Canada. Geometric means were calculated where original data were available. Otherwise the data, including arithmetic means as given by the references, are cited. The data from the present study are hourly values whereas the other data were derived from composited samples of varying time periods. It should also be noted that data from more than one treatment plant are cited for some of the locations.

Total chromium and zinc concentrations were appreciably higher than those of the other metals in Edmonton sewage. With the exception of copper concentrations in Vancouver, dry weather metal concentrations in Edmonton sewage were generally considerably higher than total metal concentrations reported from other cities of comparable size in western Canada. Total concentrations of chromium and nickel are particularly high in Edmonton municipal wastewaters. However, apart from chromium, total metal concentrations in Edmonton were considerably lower than

Table 5.2 Total Metal Concentrations in Untreated Municipal Sewage in Canada

Location	Metal Concentration (mg/L) Cd	Cr	Cu	Ni	Zn	Reference
Edmonton	0.0008-0.0092 (0.0026)	0.095-4.5 (0.254)	0.039-0.295 (0.090)	0.015-0.300 (0.042)	0.080-0.84 (0.19)	This study
Edmonton	0-0.034 (0.005)	0-6.29 (0.303)	0.03-0.18 (0.092)	0-0.132 (0.038)	0.07-0.85 (0.252)	Brown, 1980
Calgary		0.002-0.044 (0.022)	0.051-0.143 (0.078)	0-0.020 (0.010)	0.075-0.240 (0.113)	McIntosh, 1980a
Calgary	0-0.009 (0.002)	0.023-1.33 (0.076)	0.059-0.176 (0.094)	0-0.054 (0.008)	0.075-0.238 (0.109)	McIntosh, 1980b
Ontario	0-0.5	0-5.0	0-4.7	0-12	0-3.0	Abbott, 1971
Ontario	0.003-0.02 [0.006]	0.01-1.64 [0.29]	0.06-0.98 [0.31]	<0.03-1.89 [0.33]	0.23-25.99 [2.40]	Oliver and Cosgrove, 1974
Ontario	0.006-0.04	0.02-1.4	0.06-1.20	<0.03-1.8	0.11-2.40	Oliver and Cosgrove, 1975
Ontario	<0.01-0.15	<0.02-7.9	0.08-1.7	0.01-4.5	0.04-8.1	Atkins and Hawley, 1978
Vancouver	<0.001-0.019		0.031-0.222 [0.160]	0.002-0.036 [0.009]	0.027-0.286 [0.128]	Koch *et al.*, 1977
Winnipeg		[0.471]	[0.157]	[0.066]	[0.565]	Carroll and Lee, 1977

( ) geometric mean values

[ ] arithmetic mean values

values reported from Ontario municipalities. Chromium concentrations in the Edmonton sewage appear to be similar to those in Ontario. It has previously been noted that total metal concentrations in Ontario municipal wastewaters are often high on a world basis (Nielsen and Hrudey, 1981), probably because of relatively high proportions of industrial wastes in those municipal wastewaters for which data were reported.

Nickel in municipal sewers originates mainly from industrial discharges and chromium can be derived from both domestic and industrial sources (Davis and Jacknow, 1975; Gurnham *et al*., 1979; Klein *et al*., 1974). Metal finishing industries and tanning operations are obvious industrial sources of these metals. Although approximately half of the electroplating and metal finishing plants in Alberta are in Edmonton, the numbers of these plants and employees in the province are small compared to those in Ontario, Quebec, and British Columbia (EPS, 1975; Holtz, 1980). Records also showed that there was only one tanning operation, employing about 80 people, in Edmonton (Bissett, 1980).

The raw sewage was sampled immediately downstream from the grit tanks and not at the inlet to the plant because industrial liquid wastes brought to the plant for disposal were dumped in the grit tanks. During the present study several trucks were seen to dump wastes into the right side grit tank. Consequently, it was of interest to determine whether total metal concentrations from the three grit tanks differed from each other. Two-way t-tests (Miller and Freund, 1977) were used for the cadmium, copper, nickel and zinc data. The chromium data, which followed a bi-modal distribution (refer Section 5.2.2), were analyzed using the non-parametric Mann-Whitney test (Miller and Freund, 1977).

The results showed that there were no significant differences in total metal concentrations between the centre and left side grit tanks. Zinc concentrations from the right side grit tank (Site A) were found to be significantly different from those in the centre and left side tanks, and cadmium concentrations from the right and left side grit tanks were significantly different ($p < 0.05$). Mean cadmium and zinc concentrations from Site A were, however, lower than those in the other two grit chambers. These results indicate differing performances of the three grit tanks. They also suggest that tanker truck wastes did not cause significant increases in influent loadings of the metals determined during the study period. The latter conclusion was reinforced by the low metal concentrations found in grab samples collected from Site A when tanker truck wastes were being dumped.

5.2.2 Temporal Variations

Total hydraulic and metal loadings to the Gold Bar Wastewater Treatment Plant for the three 24-hour periods sampled during the survey are tabulated in Table 5.3. Loadings for metals which showed no significant

Table 5.3 Hydraulic and Metal Loadings to the Gold Bar Wastewater Treatment Plant for Three 24 h Periods (0900 to 0900 h)

Time	Loading					
	Hydraulic (ML/d)	Metal (kg/d)				
		Cd	Cr	Cu	Ni	Zn
8 - 9/6/80 (Sun) (Mon)	240	0.87	42	18	7.9	48
10 - 11/6/80 (Tues) (Wed)	280	1.2	140	36	15	120
12 - 13/6/80 (Thurs) (Fri)	280	1.1	220	34	17	80

concentration differences between grit tanks were calculated as three times the sum of the hourly loadings from the right side grit tank for the chosen time periods. Cadmium and zinc loadings, which differed significantly between grit tanks, were calculated from:

$$\text{Total loading} = (\Sigma\text{RS loading}) + \left[(\Sigma\text{RS loading}) \cdot \frac{C_{GMC}}{RS_{GMC}}\right] + \left[(\Sigma\text{RS loading}) \cdot \frac{LS_{GMC}}{RS_{GMC}}\right] \qquad 5.2$$

where RS = right side

LS = left side

C = centre

GMC = geometric mean concentration

Missing data were calculated as the means of the values preceding and following the missing value.

Although the hydraulic loadings did not differ markedly from day to day, metal loadings for Sunday-Monday were generally much smaller than for the two weekday periods. With the exceptions of chromium and zinc, the metal loadings for the two weekday periods were quite similar. These results imply that some major waste metal sources do not discharge on a continuous basis.

Hourly influent flows and total metal concentrations from Site A are shown in Figures 5.2 to 5.6. Comparison of these figures shows that distinct diurnal variations occurred and that concentration and flow peaks often coincided. Correlation coefficients between total

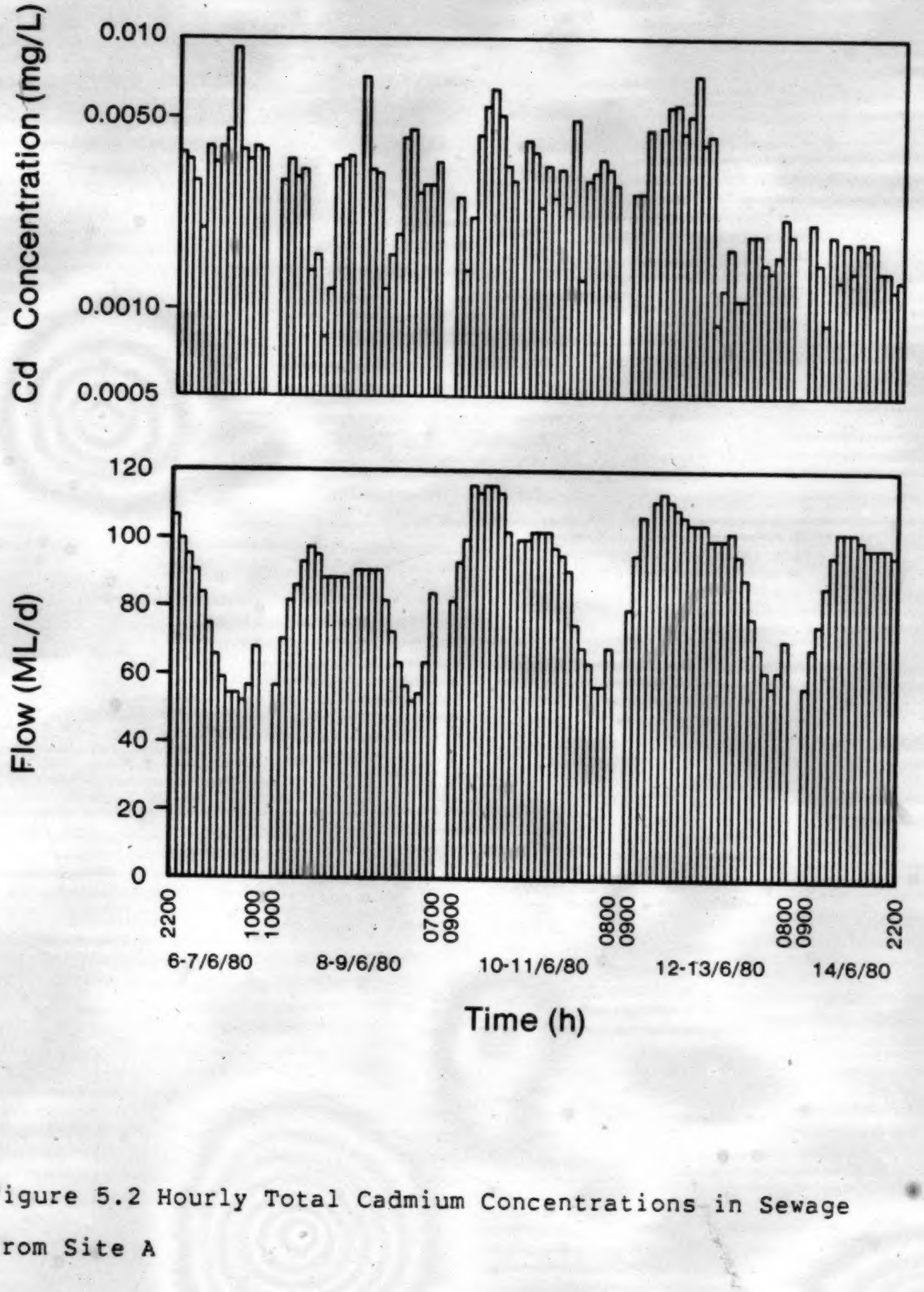


Figure 5.2 Hourly Total Cadmium Concentrations in Sewage from Site A

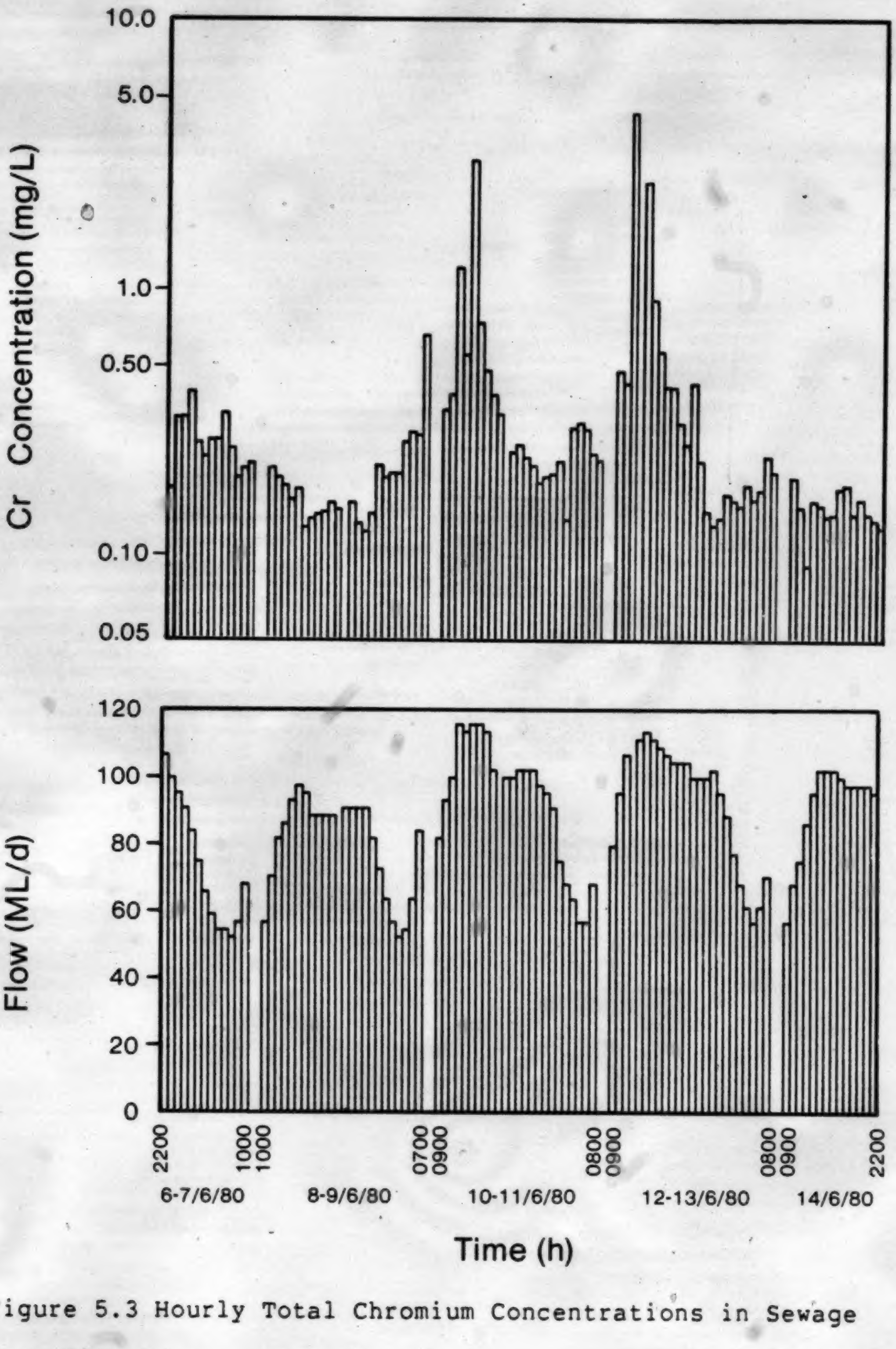


Figure 5.3 Hourly Total Chromium Concentrations in Sewage from Site A

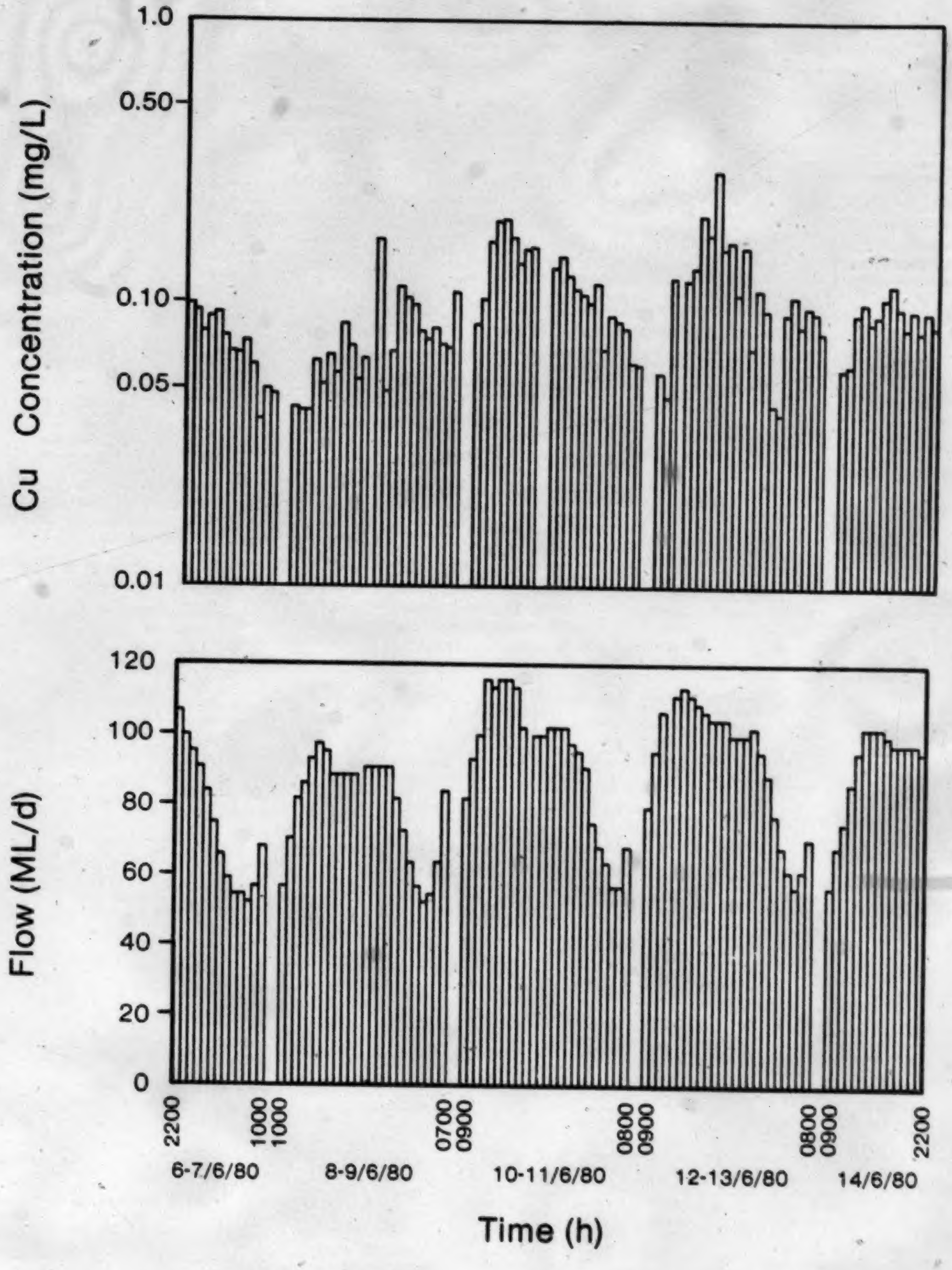


Figure 5.4 Hourly Total Copper Concentrations in Sewage from Site A

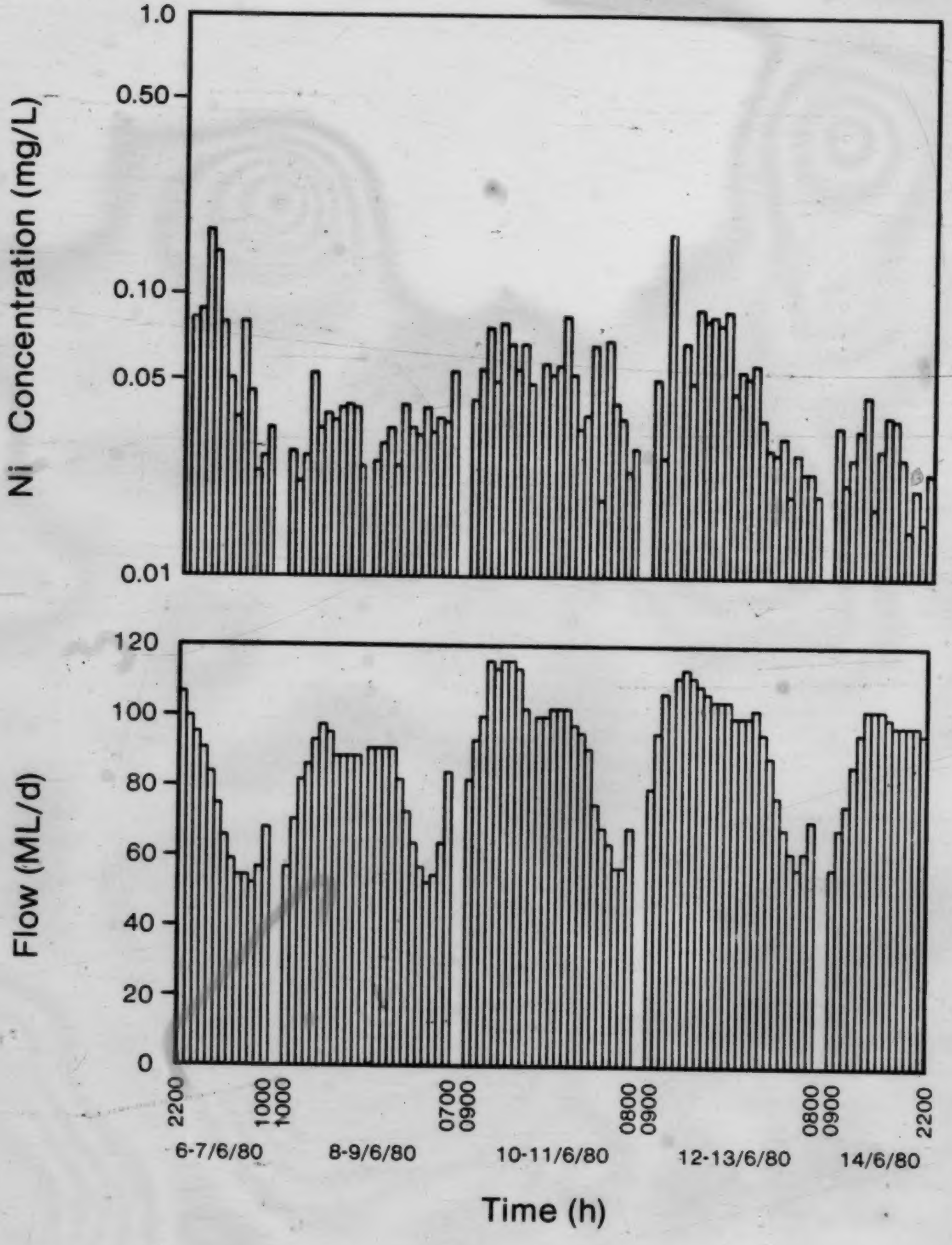


Figure 5.5 Hourly Total Nickel Concentrations in Sewage from Site A

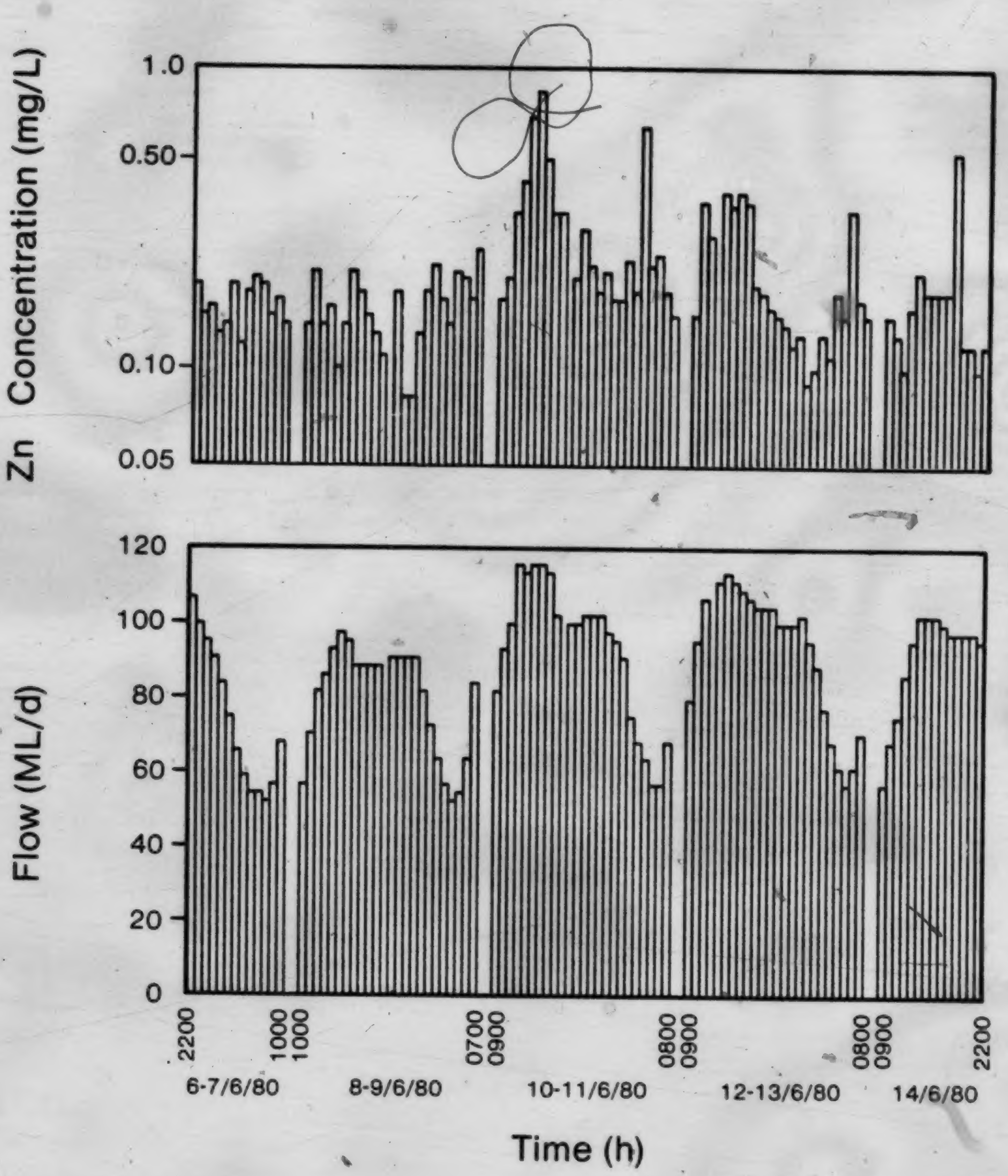


Figure 5.6 Hourly Total Zinc Concentrations in Sewage from Site A

concentrations and flows were significant ($p < 0.05$) except for cadmium. Since higher flows tend to coincide with increased urban activities, the correlation of metal concentrations may actually have been with the latter. Peak flows of about 115 ML/d were measured from Site A during the afternoon hours and these were approximately twice the early morning flows. Weekend peak flows were 10% to 12% lower than those during weekdays.

With the exception of chromium, total metal concentrations varied by approximately one order of magnitude. The variations in chromium concentrations were five times larger. The occurrence of narrow chromium peaks at approximately noon during weekdays strongly indicates the possibility of industrial chromium wastes being discharged on a batch basis during weekday mornings.

Copper exhibited peaks during early to mid-afternoon and evening hours. The similarities in shapes and temporal positions of the concentration peaks with the flow peaks suggests that much of this metal is derived from domestic sources. Industrial wastewater flows are a relatively small proportion of total Edmonton sewage flows (Hrudey, 1982) and thus would not strongly influence flow peaks. Edmonton tap water is slightly alkaline (pH = 7.9 to 8.3) and aggressiveness index (as defined by AWWA (1981)) data indicate that it is non-aggressive or only very slightly aggressive (Walker, 1981). These data suggest that copper plumbing is probably only a small source of copper in municipal sewage.

Temporal variations for cadmium, nickel and zinc, are more complex. Although the temporal positions of many of the peaks suggest domestic sources, the presence of concentration peaks at times of low flows also suggests low volume high strength industrial discharges.

Log concentration cumulative frequency plots of these data are shown in Figures 5.7 to 5.11. The chromium data were not log-normally distributed. Concentrations for this metal exhibited a bi-modal distribution because of the few very large concentrations measured. The other data, however, showed excellent agreement with a log normal model.

5.2.3 Metal Distributions Between Soluble and Particulate Phases

Table 5.4 summarizes ratios of soluble/total metal concentrations for all raw sewage and effluent samples. The soluble metal is defined as that which passes through 0.45 µm membrane filters.

Inspection of the number of data with values less than or equal to 1.0 shows that, despite the care taken in cleaning equipment and sample handling, filter contamination was an important factor. In the absence of contamination the soluble concentration can obviously not be larger than the total concentration. Filtered nickel and zinc values were particularly prone to severe contamination whereas cadmium, chromium and copper results were not.

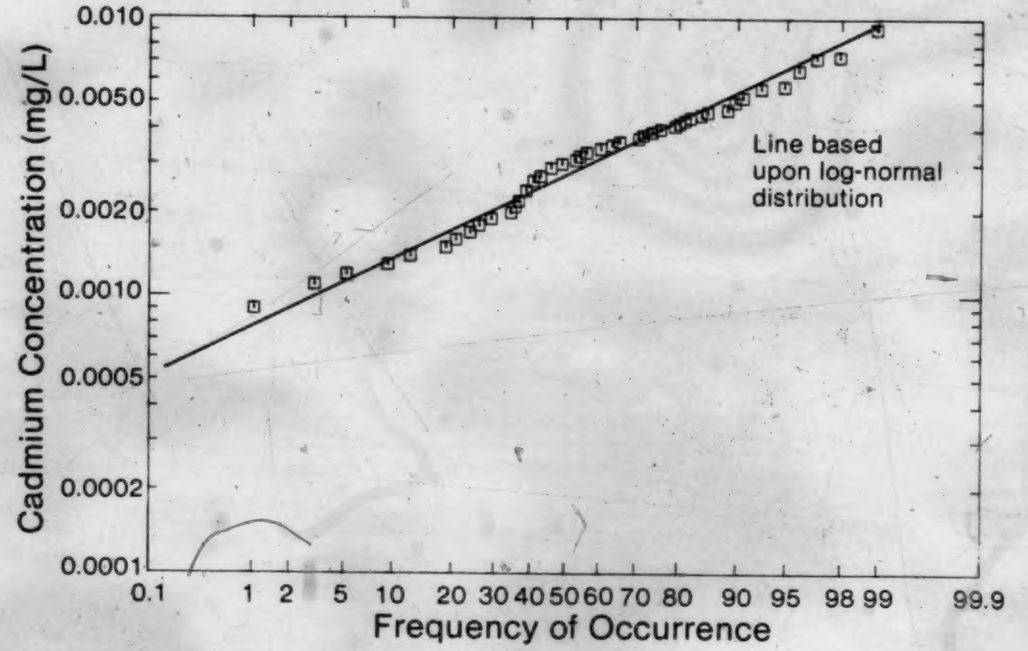


Figure 5.7 Concentration Cumulative Frequency Plot for Total Cadmium

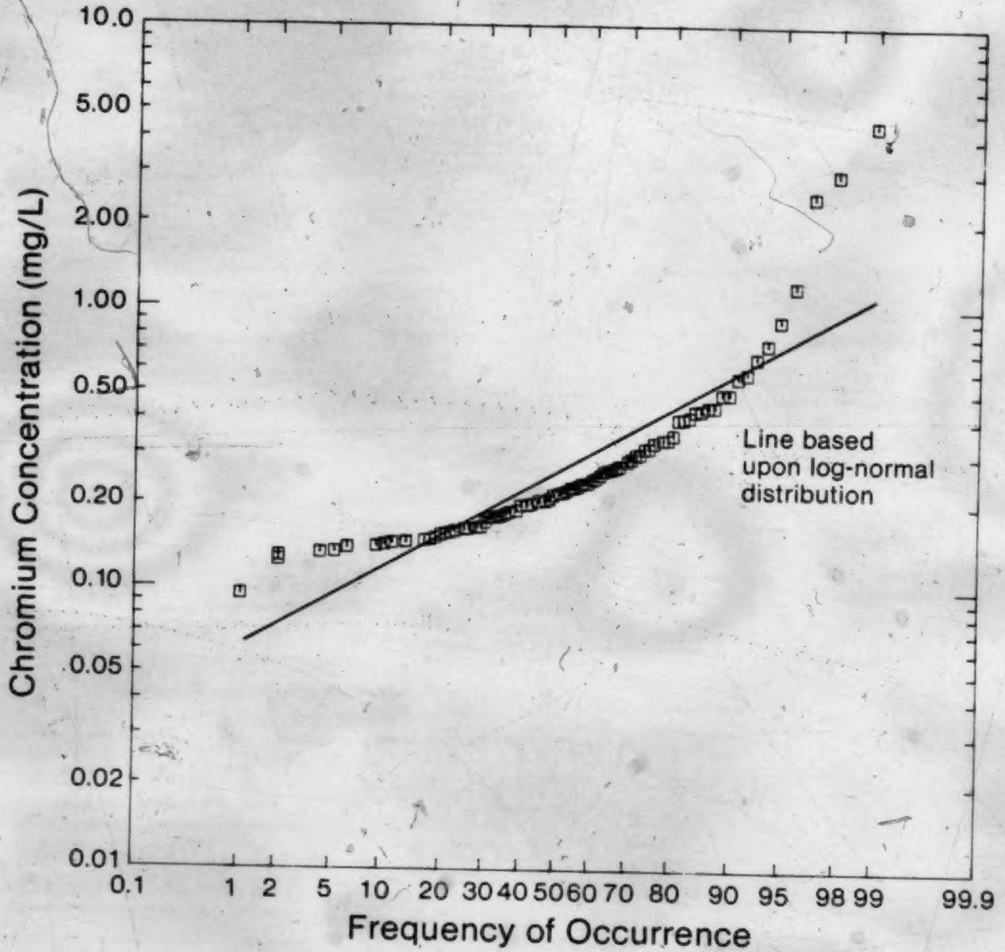


Figure 5.8 Concentration Cumulative Frequency Plot for Total Chromium

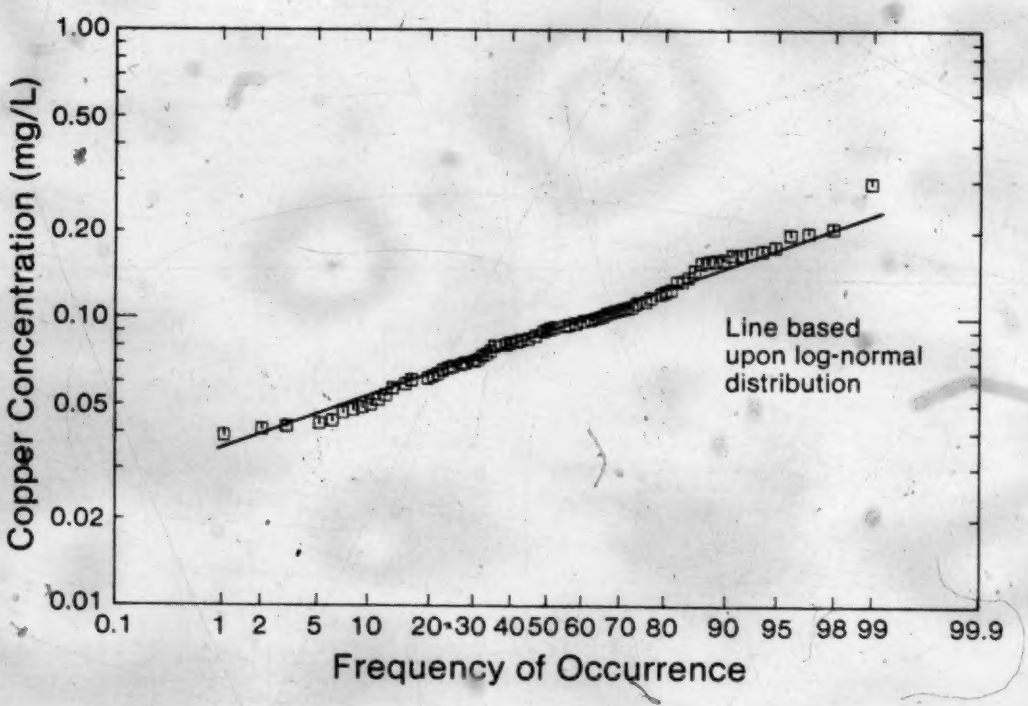


Figure 5.9 Concentration Cumulative Frequency Plot for Total Copper

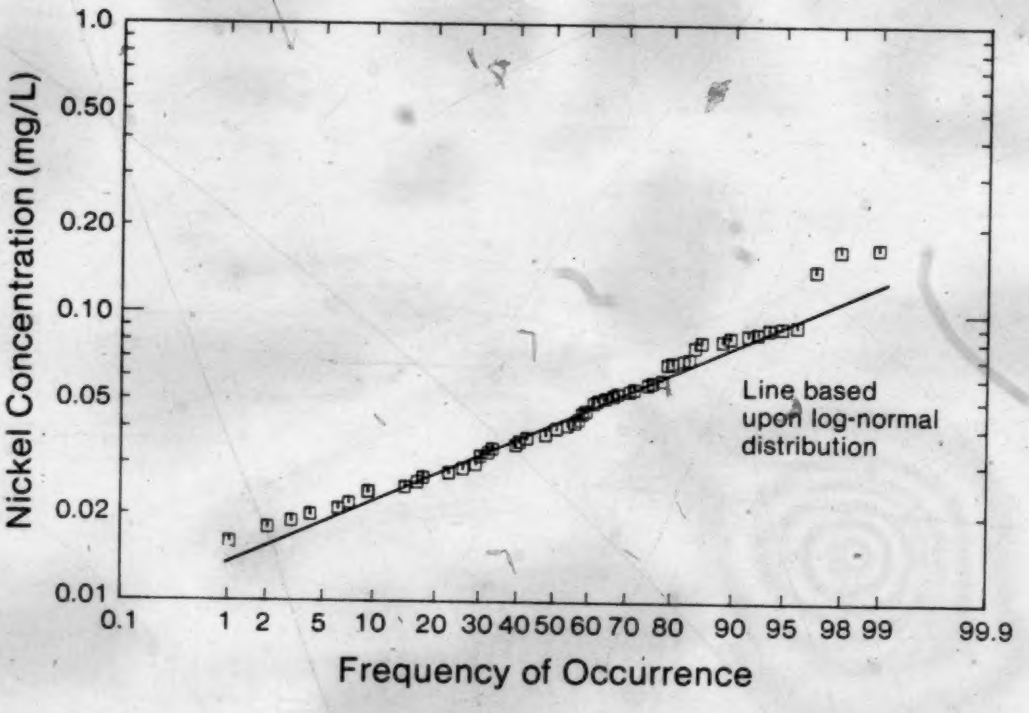


Figure 5.10 Concentration Cumulative Frequency Plot for Total Nickel

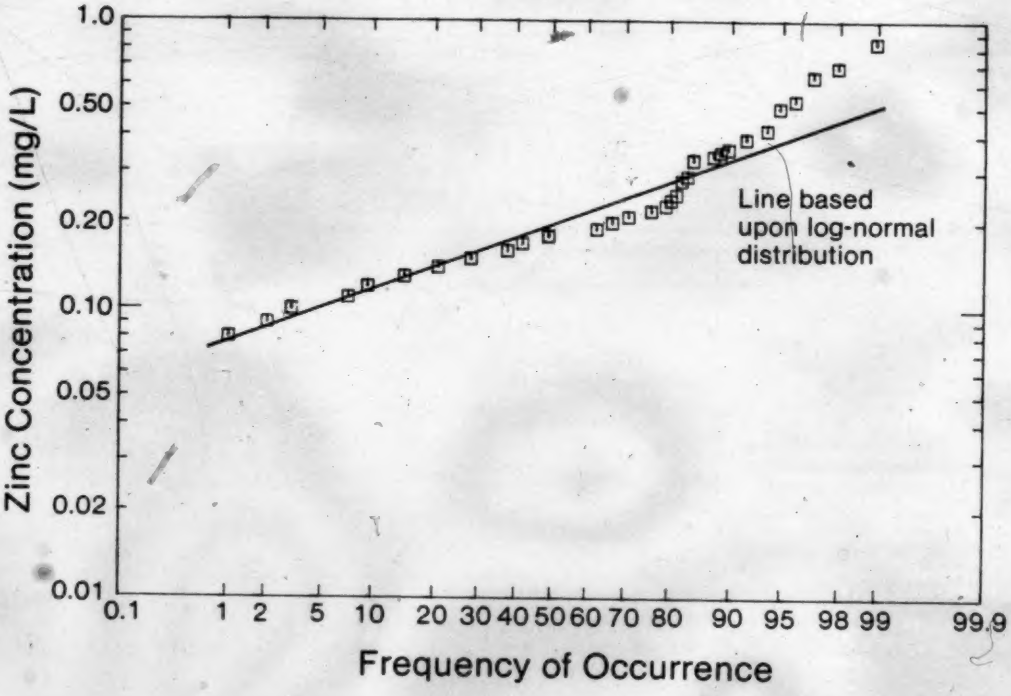


Figure 5.11 Concentration Cumulative Frequency Plot for Total Zinc

Table 5.4 Summary of Soluble/Total Metal Concentration Ratios for all Sewage Samples

	Metal Ratio				
	Cd	Cr	Cu	Ni	Zn
Total No. of ratios	149	149	148	144	149
No. with values ≤ 1.0	147	149	148	93	94

These results for copper and nickel were confirmed by analyzing digested membrane filters which had been acid washed. They were found to contain insignificant amounts of copper (< 0.001 mg/g) and large amounts of nickel (> 0.04 mg/g). It is possible that all of the filtered nickel and zinc samples were contaminated to some extent. Contamination problems with filtration through membrane filters have been described in the literature (Benes and Steinnes, 1974; Marvin *et al.*, 1970). This highlights the necessity of carefully checking even widely used sample preparation procedures to avoid spurious results, paricularly when working at low trace concentrations.

Table 5.5 shows soluble/total metal ratios in raw sewage, primary effluent and final effluent. Only ratios ≤ 1.0 were included. The nickel and zinc ratios are tentative in view of the filter contamination previously discussed. With the exceptions of nickel and zinc, the metals in the raw sewage existed largely in the particulate phase. The result for zinc was in contrast to published data which has shown zinc in raw sewage to be mainly insoluble (Oliver and Cosgrove, 1974; Patterson *et al.*, 1975). Metals in the final effluent were mainly soluble, which is consistent with available information (Chen *et al.*, 1974; Nomura and Young, 1974; Oliver and Cosgrove, 1974).

The soluble/total metal ratios for cadmium, chromium and copper increased markedly at the primary and secondary treatment stages, whereas nickel and zinc ratios only showed

Table 5.5 Soluble/Total Concentration Metal Ratios for Raw Sewage, Primary Effluent and Final Effluent

	Metal Ratio[1]				
	Cd	Cr	Cu	Ni	Zn
Raw sewage					
range	0.00-1.0	0.00-0.40	0.00-0.25	0.32-1.0	0.00-1.0
median	0.06	0.09	0.04	0.70	0.75
Primary effluent					
range	0.06-0.80	0.15-0.38	0.15-0.64	0.04-1.0	0.44-1.0
median	0.22	0.18	0.38	0.97	0.88
Final effluent					
range	0.29-1.0	0.35-0.90	0.40-0.82	0.06-1.0	0.32-1.0
median	0.75	0.55	0.67	0.97	0.85

(1) Only for ratios with values less than or equal to 1.0 (refer Table 5.4)

increases in the primary effluent samples. These changes suggest that nickel and zinc, in contrast to the other metals considered, were not removed during primary sedimentation.

5.2.4 Removal Efficiencies

Removals were calculated by comparing individual final and primary effluent loadings with the appropriate hourly raw sewage loadings (calculated using equation 5.2) taking the hydraulic retention times into account. The retention times for primary treatment and for the entire plant were estimated to be 1 to 2 h and 9 to almost 13 h respectively during the study period. The digester supernatant was not included in the calculations because this was a very minor flow (< 1.0 ML/d) compared to the raw sewage. In addition, metal concentrations in the digester supernatant were generally less than 10 times greater than those in the raw sewage. The data for the overall and primary treatment corresponded to different time increments and are not directly comparable because sampling times at the final and primary effluent sites could not be staggered according to hydraulic retention times.

Table 5.6 shows removal efficiencies based on 4 and 9 data sets for overall treatment and primary treatment respectively. Overall removal efficiencies for cadmium, chromium and copper were high and those for nickel and zinc were variable and generally low. Although removal

Table 5.6 Metals Removal at Various Stages Through the Gold Bar Wastewater Treatment Plant

	% Removal				
	Cd	Cr	Cu	Ni	Zn
Total treatment					
Range	83-96	81-97	88-98	0-80	4-75
Geometric Mean	92	92	93	43	54
Primary treatment					
Range	0-87	42-88	38-77	0-81	0-63
Geometric Mean	39	68	60	30	44

efficiencies of nickel are normally low in activated sludge plants, zinc is generally removed efficiently (refer Section 2.1.4.1).

It also appears that with the exception of cadmium, the metals were predominantly removed by primary sedimentation. The ratios for mean removal efficiency for primary treatment/mean overall removal efficiency were 0.42 for cadmium and 0.64 to 0.81 for the other metals. This is not entirely consistent with the soluble/total metal ratios in the raw sewage and may be related to the arbitrary nature of the filtration process. It could also be caused by sorption of soluble metal fractions onto particulate organic material in the primary sedimentation tank in addition to physical settling and entrapment of non-soluble metal fractions. Approximately 3.5% of the activated underflow sludge (0.6-0.8 ML/d) from each of the the five secondary clarifiers was wasted to the primary sedimentation tank daily. Calculations showed that the wasted activated sludge increased the average solids loading in the primary clarifier by approximately 30% during June, 1980.

Table 5.7 summarizes metal concentrations in the primary and final effluent, and in the sludge samples measured during the survey.

Mean (geometric) cadmium, copper, nickel and zinc concentrations in the primary effluent met the recommended objectives for Canadian drinking water sources (Environ. Can., 1979) and were lower than the maximum acceptable

Table 5.7 Metal Concentrations in Treated Wastewaters and Sludges

Waste	Metal Concentration (p.p.m)(1)				
	Cd	Cr	Cu	Ni	Zn
Wastewaters					
Primary effluent	0.0010-0.0046 (0.0018)	0.037-0.17 (0.074)	0.030-0.081 (0.045)	0.015-0.65 (0.036)	0.13-0.28 (0.18)
Final effluent	0.0001-0.0014 (0.0003)	0.010-0.035 (0.018)	0.008-0.015 (0.012)	0.018-0.54 (0.042)	0.12-0.58 (0.20)
Sludges					
Mixed liquor	11.2-183 (25.1)	660-860 (765)	166-283 (224)	47-198 (93)	300-920 (452)
Return activated sludge	12.4-16.2 (13.4)	790-1020 (880)	187-278 (234)	84-130 (107)	530-880 (660)
Primary sludge	11.2-32.0 (14.7)	910-1910 (1160)	225-1586 (381)	71-176 (105)	630-830 (720)
Digested sludge	19.2-204 (33.0)	990-1240 (1140)	189-363 (258)	58-115 (80)	650-770 (700)

(1) Units are mg/L for wastewaters and mg/kg (dry weight) for sludges

( ) geometric means

concentrations for Canadian drinking waters (Dept. Nat. Health and Welfare, 1978). The mean chromium concentration exceeded these guidelines. Geometric mean metal concentrations in the final effluent were very low and did not exceed the maximum levels allowed in drinking water.

The digested sludge values are in agreement with previous Edmonton sludge data on file at Alberta Environment. None of the geometric mean concentrations exceeded the maximum values recommended by Chaney (1973) for sludges applied to agricultural lands, although the nickel value was close to the recommended maximum concentration of 100 mg/kg.

5.3 SUMMARY

The results of this field study confirmed one of the conclusions drawn from the literature review; namely that of the metals studied, nickel is most poorly removed in activated sludge treatment plants.

Furthermore, nickel concentrations in Edmonton sewage have been particularly high compared to data from other large cities in Western Canada. These conclusions led to the choice of nickel as the metal to be studied during the remainder of the research program.

These results also provided the basis for relevant experimental design in subsequent work, particularly with respect to using total nickel concentrations typically found in Edmonton sewage. It was considered important to work at concentrations typical of municipal sewage because published studies on metal uptake by activated sludge have generally used much higher concentrations (up to 1000 mg/L). They consequently do not provide information that is directly applicable to "real-world" situations.

6. DEVELOPMENT OF ION EXCHANGE METHOD FOR FREE NICKEL ION CONCENTRATIONS

This chapter presents the theory, experimental procedures and method verification for the determination of free nickel ion (hereafter called Ni^{2+}) concentrations. Experiments were carried out with standard nickel and synthetic solutions containing nickel and model ligands. Both batch and flow through column equilibration methods were used.

The Schubert approach was adopted because, as previously demonstrated, it is considerably easier to use on a routine basis than other ion exchange methods. Furthermore, a strong acid cation exchange resin was used because its ion exchange capacity is independent of pH. An underlying rationale in choosing ion exchange together with atomic absorption spectroscopy, in preference to a speciation technique such as voltammetry, was its relatively inherent simplicity. In addition, more environmental laboratories have atomic absorption spectrophotometers than polarographic equipment and the use of ion exchange involves readily-obtainable glassware and reagents.

6.1 THEORY

6.1.1 Equilibria

The complexation equilibrium for a divalent cation, M^{2+}, which forms a complex, ML_2, with ligand, L^-, is as follows:

$$M^{2+} + 2L^- \overset{\beta_2}{\rightleftharpoons} ML_2 \qquad 6.1$$

Ligand L^- may be the conjugate base of a weak acid. For simplicity, equation 6.1 is the only complexation equilibrium represented. In principle, any number of different kinds of ligands, and both lower and higher metal/ligand ratio species than ML_2 can be accommodated without any modification of the final equations given below.

In the presence of a sodium-form strong acid type cation exchange resin, RNa, the metal cation is also involved in the equilibrium:

$$M^{2+} + 2RNa \overset{K_{IE}}{\rightleftharpoons} R_2M + 2Na^+ \qquad 6.2$$

The equilibrium constants corresponding to equilibria 6.1 and 6.2 are:

$$\beta_2 = \frac{[ML_2]}{[M^{2+}]\,[L^-]^2} \qquad 6.3$$

and

$$K_{IE} = \frac{[R_2M]\,[Na^+]^2}{[M^{2+}]\,[RNa]^2} \qquad 6.4$$

Concentrations are used rather than activities because all measurements are made at constant ionic strength (see

Assumption 1, below). The distribution coefficient, λ_o, of the species M^{2+} is a constant under the experimental conditions used and is characteristic of the metal. It is given by:

$$\lambda_o = \frac{[R_2M]}{[M^{2+}]} \qquad 6.5$$

$$= \frac{[R_2M]^*}{[M^{2+}]^*} \qquad 6.6$$

$$= K_{IE} \cdot \frac{[RNa]^2}{[Na^+]^2} \qquad 6.7$$

The superscript (*) refers to concentrations measured in the presence of resin. Rearranging equation 6.5 gives:

$$[M^{2+}] = \frac{[R_2M]}{\lambda_o} \qquad 6.8$$

This equation is used to calculate free metal ion concentrations in all cases. The way in which equation 6.8 is used, however, varies according to whether a batch or flow through method is used.

6.1.2 Assumptions

Four assumptions are made in the use of equation 6.8.

Assumption 1. All blank, standard and sample solutions are "swamped" with the same concentration of inert electrolyte.

Addition of a large excess of electrolyte to all blanks, standards and samples is required to provide the same $[Na^+]$, and therefore the same λ_o, for M^{2+}. Since dissolved salt concentrations in sewage are typically less than 0.01 M (W.P.C.F., 1977), a concentration of $\geq$ 0.1 M added electrolyte is sufficient to "swamp" the system.

While the need to "swamp" the electrolyte present in the initial sample provides a practical lower limit to the amount of electrolyte added, an upper limit is imposed by the desire to retain a high selectivity of the resin for the divalent cation M^{2+} over monovalent cation ML^+, and also to minimize electrolyte sorption of anionic nickel-ligand species. Raising the ionic strength, μ, of sewage samples will alter M^{2+} concentrations somewhat because of its effect on ionic activity coefficients of metal and ligand species. Where suspended colloidal particles are present, a change in μ may also alter the amount of M^{2+} adsorbed to them (Guy and Chakrabarti, 1975). Calculations showed that these effects will normally bring about changes in M^{2+} concentration of less than one or two-fold.

Assumption 2. Equivalents of resin exchange sites are much greater than equivalents of sample metal ion sorbed onto the resin at equilibrium, i.e. $[RNa] >> [R_2M]$.

In the batch method, both the use of a sufficiently large weight of resin and the choice of ionic strength, i.e. concentration of $NaNO_3$, guarantees the validity of this assumption. In the flow through method, $[R_2M]$ is controlled by the ionic strength. Taken together, Assumptions 1 and 2 provide for "trace" conditions of ion exchange at which λ_o

can be considered constant (Helfferich, 1962).

Assumption 3. The only species of the sample metal that is sorbed onto the resin is M^{2+}.

This assumption is not likely to be rigorously met because cationic metal complexes possessing equal or lower charge than the free metal ion, such as ML^{+} and $M(NH_3)_x^{2+}$, will also undergo ion exchange (Fronaeus, 1951; Helfferich, 1962). Assumption 3 is common to all ion exchange speciation methods when applied to real samples of ill-defined composition. It is likely to lead to relatively small errors for two reasons. First, in complex aqueous samples such as municipal sewage in which the pH is generally higher than 7, the principal ligands are likely to be polydentate and/or to carry a multiple negative charge. Consequently, cationic metal-ligand species are unlikely to represent a significant fraction of the metal concentration except in unusual samples containing high concentrations of neutral ligands such as NH_3. Typically, $[NH_3]$ is less than 10^{-5} $\underline{M}$ (W.P.C.F., 1977). Second, the exchanger generally has a lower affinity for species of lower charge (e.g. for ML^{+} compared to M^{2+}), especially at low ionic strength (Achilles *et al.*, 1977; Helfferich, 1962; Schubert and Lindenbaum, 1952).

Sorption by the exchanger of neutral species containing the metal ion of interest (e.g. ML_2) and of co-ion species (e.g. ML_x^{-}) is also ignored as a consequence of Assumption 3. This is reasonable since nonelectrolyte sorption and electrolyte sorption are much less favored processes than ion exchange even at solution ionic strengths as high as 0.3 M.

Assumption 4. No L-containing species (e.g. HL) are sorbed onto the resin. This assumption only applies to the batch method.

The effect of this type of sorption is to cause the free ligand concentration, $[L^-]$, to be dependent on the weight of resin used in the batch method. This assumption is probably valid because ligands are likely to be negatively charged at pH values commonly found in municipal sewage, and uncharged ligands, such as NH_3, are present at low concentrations (refer previous discussion about Assumption 3).

6.1.3 Batch Method

The total (formal) concentration of a metal, which includes all metal-containing species, is first measured in the sample solution. A known volume, V, of sample is then equilibrated in a flask with a known weight, G, of resin in the Na-form, and the total metal concentration is again measured in the solution phase. Using symbols as defined in Section 6.1.1, the total moles of metal, T_M, and ligand, T_L, in the flask are given by the following expressions:

$$T_M = T_{M,S} + T_{M,R} \tag{6.9}$$

$$= [M^{2+}]^* \cdot V + [ML_2]^* \cdot V + [R_2M]^* \cdot G \tag{6.10}$$

$$= [M^{2+}]\cdot V + [ML_2)\cdot V \qquad 6.11$$

$$T_L = [L^-]^*\cdot V + 2[ML_2]^*\cdot V \qquad 6.12$$

where $T_{M,S}$ is total moles of metal in the resin-equilibrated sample solution; and

$T_{M,R}$ is moles of metal on the resin.

A species-independent distribution ratio, λ, of the metal can be calculated using the expression:

$$\lambda = \frac{T_{M,R}/G}{T_{M,S}/V} \qquad 6.13$$

where $T_{M,S}$ is known from the total metal concentration determined in the sample solution after resin equilibration; and

$T_{M,R}$ is obtained from equation 6.9.

The value of the free metal ion distribution coefficient, λ_o, is calculated in a similar manner to λ by performing the above-described measurements on a metal containing solution in the absence of any ligand (i.e. where all of the metal in solution is free). In this case $\lambda = \lambda_o$.

Three cases can be distinguished based on the degree of metal ion buffering in the sample solution (Fulton and Kratochvil, 1980).

Case 1. If the formal concentration of ligand is much larger than that of metal and if most of the metal is present in the form of labile metal-ligand complexes, then the solution is well buffered with respect to the free metal ion. The relatively small amount of metal taken up by the ion exchanger does not alter $[M^{2+}]$ significantly from its initial concentration in the sample. It is, of course, the free metal ion concentration in the original sample, $[M^{2+}]$, which is the object of the study in every case.

Case 2. If the formal concentration of ligand is much larger than that of metal, but the metal is not largely present as labile complexes, the solution is not well buffered in metal ion. Under these conditions $T_L = [L^-] \cdot V$. Furthermore, λ is a constant and for the simple example of complexation chosen for illustration in equation 6.1, it is given by:

$$\lambda = \frac{[R_2M]}{[M^{2+}] + [ML_2]} \qquad 6.14$$

$$= \frac{[R_2M]^*}{[M^{2+}]^* + [ML_2]^*} \qquad 6.15$$

Substituting for $[R_2M]$ and $[ML_2]$ from equations 6.5 and 6.3 respectively, gives:

$$\lambda = \frac{\lambda_o}{1 + \beta_2 [L^-]^2} \qquad 6.16$$

$$= \text{constant, because } [L^-] \text{ is constant}$$

Equations 6.14 and 6.16 can readily be generalized for cases where additional ligands and complexes are also present. Except where polynuclear complexes are present, λ will still be a constant.

The free metal ion concentration measured in the presence of resin, $[M^{2+}]^*$, can be related to the free metal ion concentration in the absence of resin, $[M^{2+}]$. Substituting for the terms $[ML_2]^*$ and $[R_2M]^*$ in equation 6.10 using equations 6.3 and 6.6 respectively, gives:

$$T_M = [M^{2+}]^* \cdot V + (\beta_2 [M^{2+}]^* [L^-]^2) \cdot V + (\lambda_o \cdot [M^{2+}]^*) \cdot G \qquad 6.17$$

Rearrangement of equation 6.17 yields:

$$\frac{1}{[M^{2+}]^*} = \frac{V}{T_M} \left(1 + \beta_2 [L^-]^2\right) + \frac{\lambda_o}{T_M} \cdot G \qquad 6.18$$

Further, substitution for $(1 + \beta_2[L^-]^2)$ from equation 6.16 gives:

$$\frac{1}{[M^{2+}]^*} = \left(\frac{V}{T_M} \cdot \frac{\lambda_o}{\lambda}\right) + \frac{\lambda_o}{T_M} \cdot G \qquad 6.19$$

Equations 6.18 and 6.19 show that the first term on the right hand side is a constant, i.e. independent of G. The value of this term is obtained by substituting for T_M, λ_o and λ from equations 6.10, 6.5 and 6.14 respectively, and setting G equal to zero, i.e. $[M^{2+}]^* \equiv [M^{2+}]$ when $G = 0$. Hence, $[M^{2+}]^*$ is related to $[M^{2+}]$ according to the following equation:

$$\frac{1}{[M^{2+}]^*} = \frac{1}{[M^{2+}]} + \frac{\lambda_o}{T_M} \cdot G \qquad 6.20$$

Equation 6.20 demonstrates that $1/[M^{2+}]^*$ is a linear function of G. In this case, where the solution is not well buffered in metal ion, the resin added takes up enough metal to perturb the equilibria existing in the initial solution, causing the M^{2+} concentration in the presence of resin to be lower than in the initial solution. The reciprocal of the intercept of the linear plot of $1/[M^{2+}]^*$ vs G is the desired quantity, $[M^{2+}]$.

If only highly inert complexes are present, the solution is totally unbuffered in M^{2+} and equation 6.20 will still yield a linear plot with intercept equal to $1/[M^{2+}]$. When the solution is well buffered in metal (Case 1), the second term on the right hand side of equation 6.20 disappears because the amount of metal taken up by the resin, $[R_2M]$, is negligible.

Case 3. If the formal concentration of ligand forming labile complexes is not much larger than that of metal, then not only is the solution poorly buffered in metal ion but also λ is not a constant. An expression for $[L^-]$ can be obtained by substituting for $[ML_2]^*$ in equation 6.12 from equation 6.10:

$$[L^-]^* \cdot V = T_L - 2\,(T_M - [M^{2+}]^* \cdot V - [R_2M]^* \cdot G) \qquad 6.21$$

Substitution for $[M^{2+}]^*$ from equation 6.6 and rearrangement gives:

$$[L^-]^* = \frac{T_L - 2\,(T_M - \lambda_o\,[R_2M]^*\cdot V - [R_2M]^*\cdot G)}{V} \qquad 6.22$$

Hence, when this expression for $[L^-]^*$ is substituted into equation 6.16:

$$\lambda = \frac{\lambda_o}{1 + \frac{\beta_2}{V}\left(T_L - 2\,(T_M - \lambda_o[R_2M]^*\cdot V - [R_2M]^*\cdot G)\right)^2} \qquad 6.23$$

$\neq$ constant, because $[L^-]^*$ depends on G (in contrast to Case 2).

Consequently, a plot of $1/[M^{2+}]^*$ vs G will not be linear. It will, however, approach linearity at low G and the intercept will still be $1/[M^{2+}]$, provided that G is not so small that Assumption 2 is no longer valid. A trivial example of this case exists when there is no ligand present in the sample, in which case equation 6.20 is valid.

6.1.4 Flow Through Column Method

The column equilibration experiment involves passing the sample solution through a known weight of resin in the Na-form until the total metal concentration in the effluent is identical to that in the column influent. The resin is thus brought to equilibrium with the unperturbed initial sample solution. That is, the sample solution in contact with the resin at equilibrium has not had any M^{2+} ions removed from its labile complexes by the resin. Passage of additional sample solution through the resin makes no further change. The concentration of metal retained on the resin is subsequently measured after elution with acid.

In this method, equation 6.8 can be used as it stands since the measured $[M^{2+}]$ is independent of the weight of resin. It does not matter whether the sample solution is well buffered or not, or even whether there is an excess of ligand over the amount of metal. Polynuclear complexes are accommodated as well as any type and number of other metal-ligand complexes. Only Assumption 3, regarding the sorption by the resin of cationic metal containing complexes, cannot be assured. However, this effect is likely to be relatively small for the reasons previously given (refer Section 6.1.2).

The value of λ_o is measured by substituting a metal solution of known concentration containing no ligands for the sample solution.

6.2 PROCEDURES

6.2.1 Choice of Electrolyte and Model Ligands

Sodium nitrate was chosen as the "swamping" electrolyte because nickel complexation by nitrate is negligible ($\log \beta = 0.4$ for formation of $NiNO_3^-$ at zero ionic strength (Smith and Martell, 1976)).

Glycyl-L-alanine (gly-ala) and EDTA were used as model ligands. EDTA was chosen because it quantitatively forms only one nickel complex, NiY^{2-}, even at very low EDTA concentrations. When EDTA is present in substoichiometric amounts the Ni^{2+} concentration is totally unbuffered. Gly-ala was chosen for three reasons:

1. Its formation constants with nickel for the formation of NiL^+ and NiL_2 complexes bracket those expected in municipal sewage (Beers, 1979). At $\mu = 0.10$ M, $\log \beta_1 = 4.08$ and $\log \beta_2 = 7.87$ (Martell and Smith, 1974).

2. The acid dissociation constants of gly-ala ($pK_1 = 3.07$, $pK_2 = 8.12$ (Martell and Smith, 1974)) are such that it provides pH buffering at the desired pH of about 8; and,

3. Gly-ala forms NiL^+ and NiL_2 complexes and can therefore be used to obtain some idea of the magnitude of the systematic errors in the measured value of $[Ni^{2+}]$ resulting from the presence of a NiL^+ complex.

6.2.2 Batch Method

Blank, nickel standard and gly-ala/nickel synthetic solutions were prepared using $NaNO_3$ solutions of specified concentrations. The pH was adjusted by bubbling CO_2 through the solutions at a rate of about 20 mL/s for about 5 s per litre of solution and adding NaOH to achieve the desired pH of about 8.0. Edmonton sewage typically has pH values of 7.6 to 8.5 (Brown, 1981). Specified weights of resin were added to 50.0 mL aliquots of the adjusted synthetic solutions in covered 125 mL conical flasks and shaken at room temperature for 4 h at 200 r.p.m. Solution pH was checked hourly and readjusted to the original value if necessary. The clear supernatants were decanted from the resin, acidified (1% HNO_3 by volume) and analyzed for total nickel ($T_{M,S}$ in equation 6.9) by GFAAS. Other portions of the initial adjusted solutions, not contacted with resin, were acidified and analyzed for total nickel (T_M). Nickel sorbed onto the resin ($T_{M,R}$) was calculated using equation 6.9. The value of λ_o was obtained by substituting a $Ni(NO_3)_2$ standard solution for the synthetic solutions in the above procedure, including the pH adjustment. At least one resin-equilibrated blank (i.e $NaNO_3$) solution was carried along with each batch of samples.

6.2.3 Flow Through Column Method

The pH of solutions prepared in $NaNO_3$ was buffered with CO_2 and adjusted with NaOH to achieve the desired pH. The pH was 7.0_0 and 8.0_0 for the EDTA and gly-ala synthetic solutions respectively. One litre aliquots of the adjusted synthetic solutions were passed through ion exchange columns containing 0.300 g of resin at the rate of 6 mL/min. Experiments were done at room temperature and up to twelve columns could be used concurrently. The resin beds were subsequently washed with 10 mL aliquots of water to remove neutral and co-ion species. The last water was blown out with slight air pressure. The nickel on the resin beds was then eluted with 50.0 mL of 2.0 M HNO_3 and the eluates analyzed for nickel by GFAAS to yield directly the amount of nickel sorbed on the resin. The value of λ_o was obtained by substituting $Ni(NO_3)_2$ standard solutions for the synthetic samples in the above procedure with pH buffered at 7.0_0 or

8.0_0 as specified. One or two aliquots of blank solution (i.e $NaNO_3$) solution were treated in the same manner as the samples and standards each time a run was made.

6.3 RESULTS AND DISCUSSION

6.3.1 Batch Method

6.3.1.1 Choice of Experimental Conditions

1. Adjustment of pH.

Since pH controls the acid-base conjugate species distribution of weak base ligand components, it influences Ni^{2+} concentrations. For this reason, the pH of all blank and sample solutions was carefully controlled.

An experiment in which 50.0 mL aliquots of 0.10 M $NaNO_3$ (unbuffered in pH, i.e. no CO_2 was added to the solutions) were shaken with and without 1.000 g resin for several hours, showed that pH values dropped from 8.0_0 (initially adjusted with NaOH) to as low as 6.1 (Table 6.1). Consideration of pKa data for carbonic acid ($pK_1 = 6.3$, $pK_2 = 10.3$ at zero ionic strength (Smith and Martell, 1976)) suggested that these depressions in pH were caused by absorption of atmospheric carbon dioxide by the samples being shaken. These data also showed that the resin had no effect on sample pH values.

An unsuccessful search was made for a pH buffer with a pKa value of about 8 which did not complex nickel significantly. Salicylamide, p-acetylphenol and m-nitrophenol had appropriate pKa values, but their stability

Table 6.1 Effect of Shaking on Blank pH Values (Batch Method)

Sample	pH at Different Shaking Times			
	1 h	1.5 h	3 h	7 h
0.10 M $NaNO_3$	6.3	6.2	6.1	6.3
0.10 M $NaNO_3$+1.00 g resin	6.4	6.4	6.3	6.3

constants for Ni complex formation were either too high or unknown. Glycyl-L-alanine also had an appropriate pKa value and known stability constants for Ni, and was subsequently used as one of the model ligands (refer Section 6.2.1).

It was decided to provide pH buffering capacity by bubbling a little CO_2 through all blanks and samples prior to pH adjustment with NaOH. Mattigod and Sposito (1977) estimated overall log stability constant values of 6.87, 10.11 and 2.14 for the formation of $NiCO_3$, $Ni(CO_3)_2^{2-}$ and $NiHCO_3^+$ respectively. The value of 6.87 for the formation of $NiCO_3$ is the same as that for the formation of solid $NiCO_3$ given by Smith and Martell (1976). Intrinsic solubilities do not appear to have been taken into account by Mattigard and Sposito (1977) and consequently the true stability constants for Ni-(bi)carbonate complexes in unsaturated solutions may be several orders of magnitude less than the values given by these authors.

In a later experiment using the flow through column method, no differences were found in λ_o values measured at pH 7.0_0 and 8.0_0. These results suggested that the added CO_2 did not affect Ni speciation in any way (refer Section 6.3.2.2).

The addition of CO_2 and NaOH was found to control pH effectively; pH values of 7.8_0 to 8.4_0 were typically measured in samples after the shaking period.

2. Shaking time

Aliquots (50.0 ml) from a bulk standard solution containing 8.52×10^{-6} $\underline{M}$ (0.500 mg/L) Ni at pH 8.0_0 and 0.10 μ were shaken with 1.000 g resin at 200 r.p.m. for periods of 30 min. to 8 h. The supernatant was analyzed for nickel after the specified equilibration times. Table 6.2 shows that the ion exchange reaction was very rapid (< 0.5 h). A shaking time of 4 h was used in all batch studies to ensure resin equilibration with all types of samples.

3. Quantity of resin

Under the experimental conditions used, K_{IE}, [RNa] and $[Na^+]$ should all be constant. Thus, from equation 6.7, the value of λ_o should not change significantly when the quantity of resin is varied.

Varying weights of resin (0.100 to 3.000 g) were equilibrated with 50.0 mL aliquots of standard Ni solution (8.52×10^{-6} $\underline{M}$ or 0.500 mg/L) in 0.10 $\underline{M}$ $NaNO_3$ at pH 8.0_0. Table 6.3 shows the measured λ_o values for the various quantities of resin used. The average value of λ_o was 1.52 L/g with a standard deviation of 0.16 L/g. This small random error demonstrated that Assumption 2 (refer Section 6.1.2) was valid irrespective of the weight of resin used between 0.100 g and 3.000 g, as long as the resin weight was accurately known.

4. Ionic strength

The effect of ionic strength, μ, was determined by equilibrating 1.000 g weights of resin with 50.0 mL aliquots of 8.52×10^{-6} $\underline{M}$ (0.500 mg/L) standard Ni solutions at pH 8.0_0 containing varying amounts of $NaNO_3$ to give ionic

Table 6.2 Effect of Shaking Time on Equilibration (Batch Method)

Shaking Time (h)	Nickel in Supernatant (mg/L)
0.5	0.019
1.0	0.020
1.5	0.019
2.0	0.022
2.5	0.021
3.0	0.022
3.5	0.021
4.0	0.022
5.0	0.020
6.0	0.021
8.0	0.020

Table 6.3 Values of λ_o as a Function of Weight of Resin (Batch Method)

Resin (g)	λ_o (L/g)
0.100	1.30
0.200	1.41
0.300	1.28
0.401	1.50
0.500	1.57
0.700	1.50
0.800	1.37
1.000	1.72
1.250	1.60
1.501	1.64
2.000	1.76
3.000	1.64

strengths of 0.010 to 0.500 M.

Figure 6.1 shows the plot of distribution coefficients, λ_o, against μ. Nickel uptake by the ion exchanger decreased rapidly as μ increased because of competition by Na^+ ions for uptake.

Ion exchange behaviour can be more rigorously examined by inspection of equation 6.7. A plot of λ_o vs. $1/[Na^+]^2$ (i.e. $1/\mu^2$) should yield a straight line of slope $K_{IE} \cdot [RNa]^2$. Figure 6.2 shows this relationship for the data plotted in Figure 6.1 fitted with the linear least squares regression line of best fit. Activity coefficient corrections were not carried out because they could only be made for the solution phase and not for the resin. The slope ± 1 standard deviation was $(1.27 \pm 0.04) \times 10^{-2}$ moles^2/L·g and the intercept (0.07 ± 0.10 L/g) was not significantly different from zero. The straight line relationship verifies the assumptions of "trace" conditions of ion exchange (refer Section 6.1.2) for the weight of resin and range of ionic strengths used.

It was considered that an added electrolyte concentration of $\geq$ 0.10 M was sufficient to "swamp" sewage samples (refer Section 6.1.2). Sodium nitrate concentrations of 0.10 M were used in order to obtain optimum nickel uptake, miminize changes in ionic activity coefficients caused by added electrolyte, minimize electrolyte sorption and retain a higher selectivity of the resin for Ni^{2+} over monovalent NiL^+ species than would occur

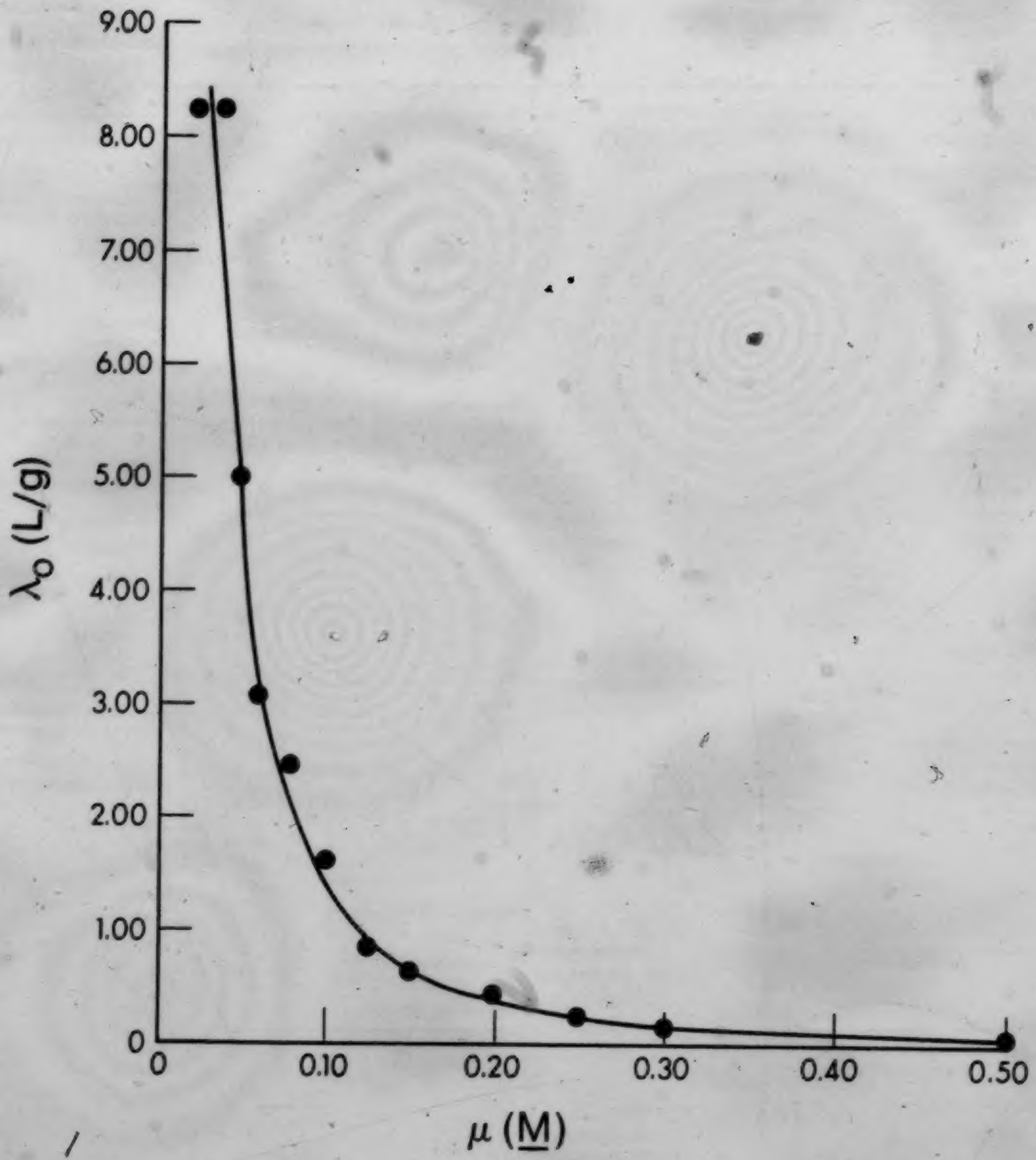


Figure 6.1 Plot of λ_o vs. μ (Batch Method)

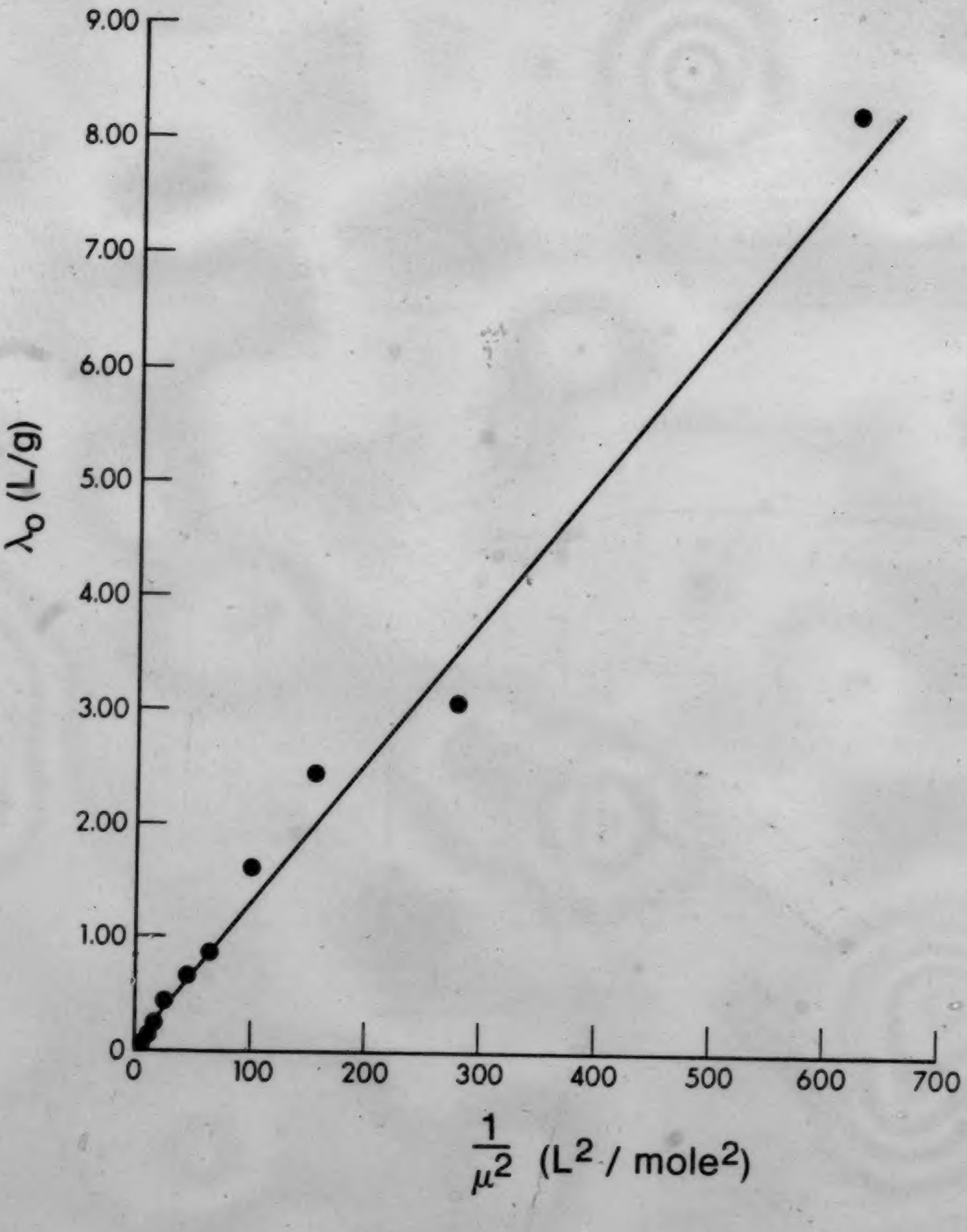


Figure 6.2 Plot of λ_o vs. $1/\mu^2$ (Batch Method)

with higher ionic strengths. The results of the previous experiment in which the quantity of resin was varied also verifies that an ionic strength of 0.10 M was sufficient to ensure trace conditions.

5. Summary of Experimental Conditions

The experimental conditions used for the batch method were:

Sample volume (mL) = 50.0
Weight of resin (g) = 0.500 or 1.000
μ (M) = 0.10
Shaking time (h) = 4

6.3.1.2 Measurement of λ_o

The value of λ_o was obtained by measuring the ion exchange uptake of nickel from a series of standard solutions containing no ligand in which Ni^{2+} concentrations were varied from 8.52×10^{-7} M (0.050 mg/L) to 8.52×10^{-5} M (5.00 mg/L). One gram weights of resin were used and sample pH values at the end of the shaking time were $8.2_0 \pm 0.2_0$ pH units.

Figure 6.3 shows a plot of nickel on the resin, RNi, against total nickel remaining in solution (i.e. $[Ni^{2+}]$) at the end of the equilibration time. The slope, i.e. λ_o, was calculated by linear regression analysis to be 1.51 ± 0.03 L/g and the intercept was $(0.04 \pm 0.04) \times 10^{-6}$ moles/g. This value of λ_o was the same as that previously obtained in the experiment in which the weight of resin was varied (refer Section 6.3.1.1). The linearity of the data also

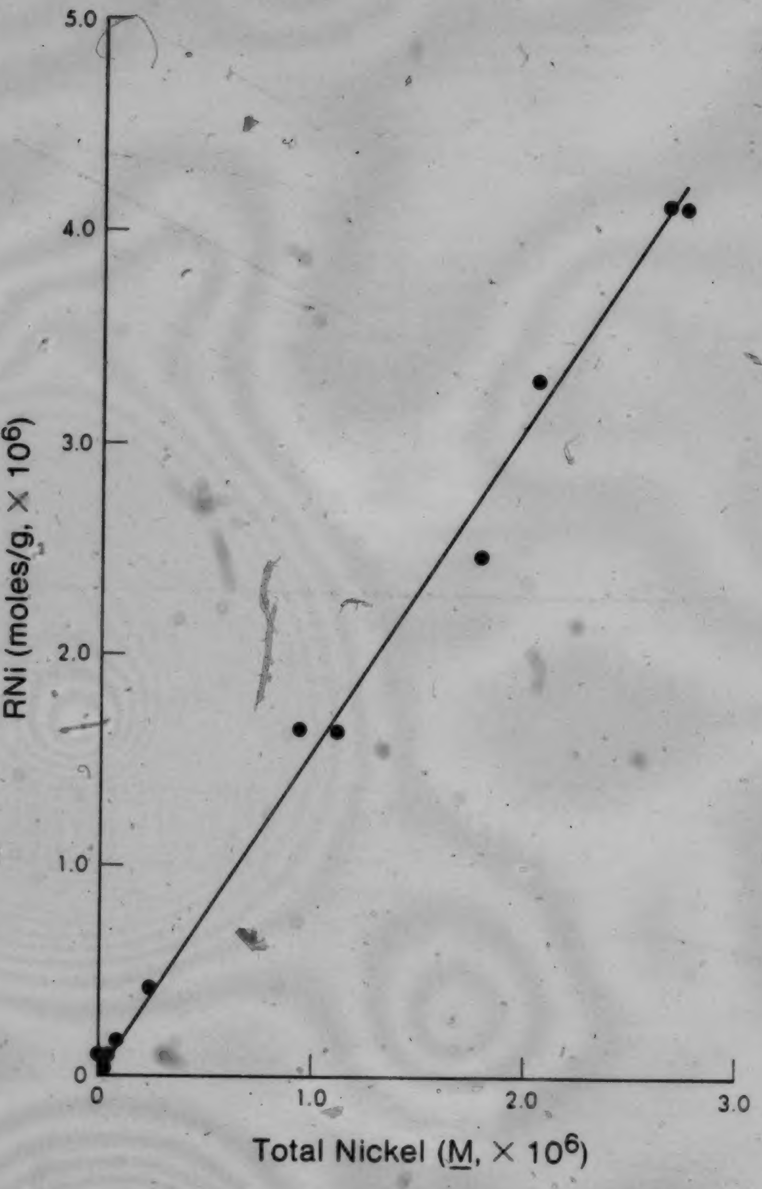


Figure 6.3 Nickel on Resin, RNi, vs. Total Nickel in Solution for Standard Nickel Solutions (Batch Method)

verified that "trace" experimental conditions were maintained for a large range of nickel concentrations using 1.000 g of resin and 0.10 M ionic strength solutions.

The analytical error in λ_o was estimated by shaking 12 replicate standard solutions containing 8.52×10^{-6} M (0.500 mg/L) Ni^{2+} with 1.000 g weights of resin at pH 8.2_0. These results are shown in Table 6.4. A mean value for λ_o of 1.62 L/g with a standard derivation of 0.15 L/g was obtained.

6.3.1.3 Measurement of $[Ni^{2+}]$ in a Synthetic Solution

The concentration of Ni^{2+}, $[Ni^{2+}]$, was measured in a synthetic gly-ala solution containing 1.70×10^{-6} M (0.100 mg/L) total nickel and 1.00×10^{-3} M (140 mg/L) gly-ala at pH 8.2_0 employing a range of resin weights, G, from 0.100 to 2.000 g. A plot of $1/[Ni^{2+}]^*$ versus G should, according to equation 6.20, yield a straight line with a slope of λ_o/T_{Ni} and an intercept equal to the reciprocal of the Ni^{2+} concentration in the unperturbed synthetic solution, $[Ni^{2+}]$.

Figure 6.4 shows the plot of $1/[Ni^{2+}]^*$ against G. These data yielded a linear plot with a slope calculated by linear regression of $(1.78 \pm 0.04) \times 10^7$ L/mole·g and an intercept of $(0.54 \pm 0.04) \times 10^7$ L/mole.

The measured slope was in very good agreement with the value of 1.77×10^7 L/mole·g predicted from equation 6.20 using $\lambda_o = 1.51$ L/g. The experimental $[Ni^{2+}]$ of $(1.8 \pm 0.2) \times 10^{-7}$ M was almost 2.5 times higher than the concentration of $(7 \pm 2) \times 10^{-8}$ M predicted using the pKa

Table 6.4 Replicate λ_o Values (Batch Method)

Sample	λ_o (L/g)
1	1.53
2	1.53
3	1.53
4	1.67
5	1.53
6	1.41
7	1.83
8	1.67
9	1.67
10	1.83
11	1.83
12	1.48

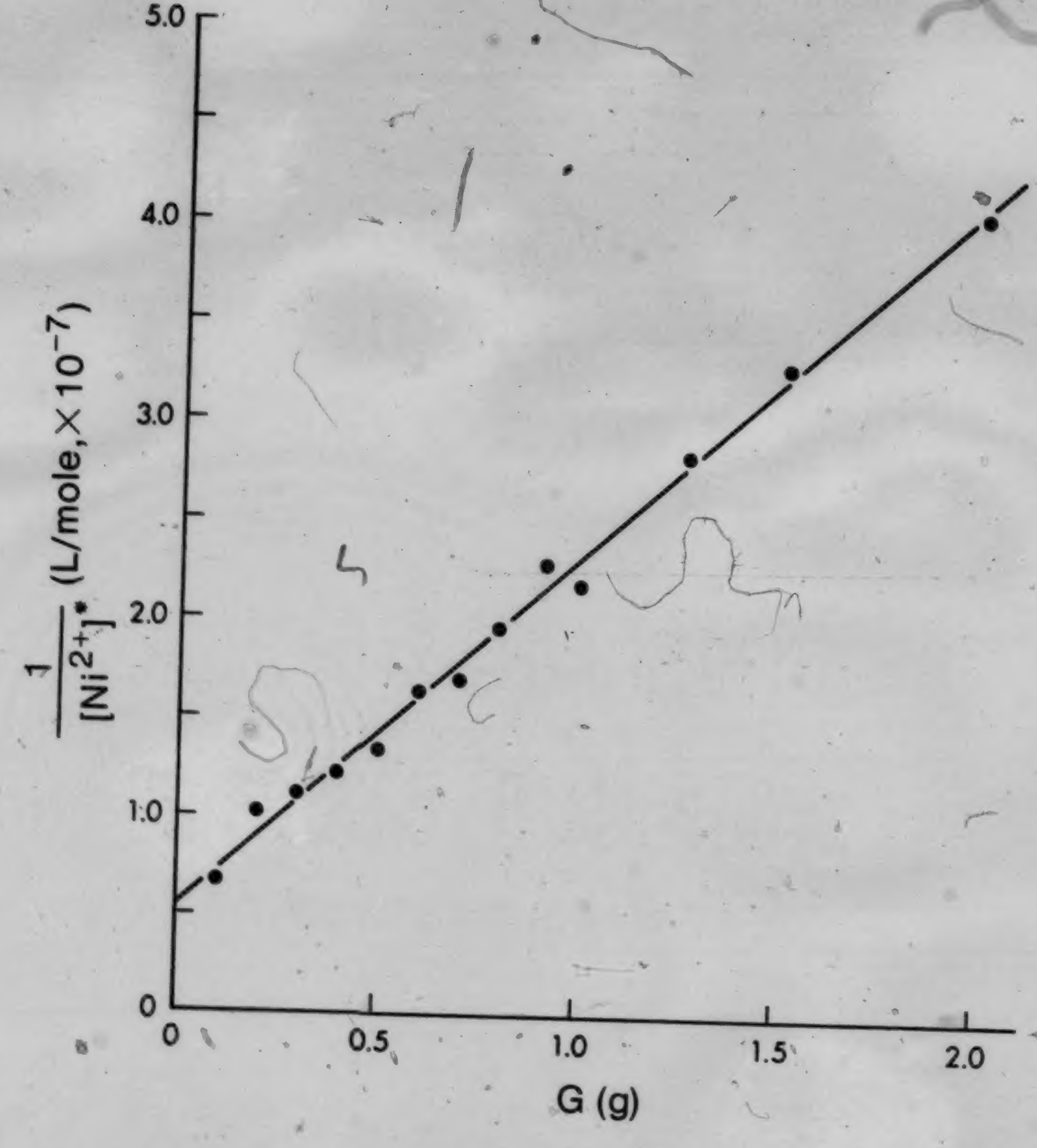


Figure 6.4 Data for Gly-Ala Synthetic Solution Plotted to Obtain [Ni^{2+}] (Batch Method)

and β values from Martell and Smith (1974) as given in Section 6.2.1.

The major sources of error in the predicted [Ni^{2+}] for this ligand system are the uncertainties in pH measurements and in the pKa and β values. The relative errors (± 1 standard deviation), using ± 0.05 in pH measurements, ± 0.03 and ± 0.02 for pKa and pKa_2 respectively (Martell and Smith, 1974), and 9 and 18% for β_1 and β_2 respectively (Sychev and Mitsul, 1967), are about 12% from pH measurements and 24% from the constants giving a total relative standard deviation of about 36%.

6.3.2 Flow Through Column Method

6.3.2.1 Choice of Experimental Conditions

1. Ionic Strength

Successive aliquots of 1.70×10^{-7} M (0.010 mg/L) and 5.11×10^{-6} M (0.300 mg/L) Ni^{2+} standard solutions, prepared in 0.10, 0.20 and 0.30 M $NaNO_3$, were passed through 0.300 g resin columns. These aliquots were analyzed directly with GFAAS. Figure 6.5 shows ratios of total Ni in the effluent/total Ni in initial standard solution, C_e/C_i, as a function of sample volume for all the solutions used.

Resin equilibration was achieved for both Ni^{2+} concentrations after the passage of about 200 mL and 500 mL of 0.30 M $NaNO_3$ and 0.20 M $NaNO_3$ solutions respectively. Complete equilibration was not achieved with the 0.10 M $NaNO_3$ solution after 2L had been passed through the resin.

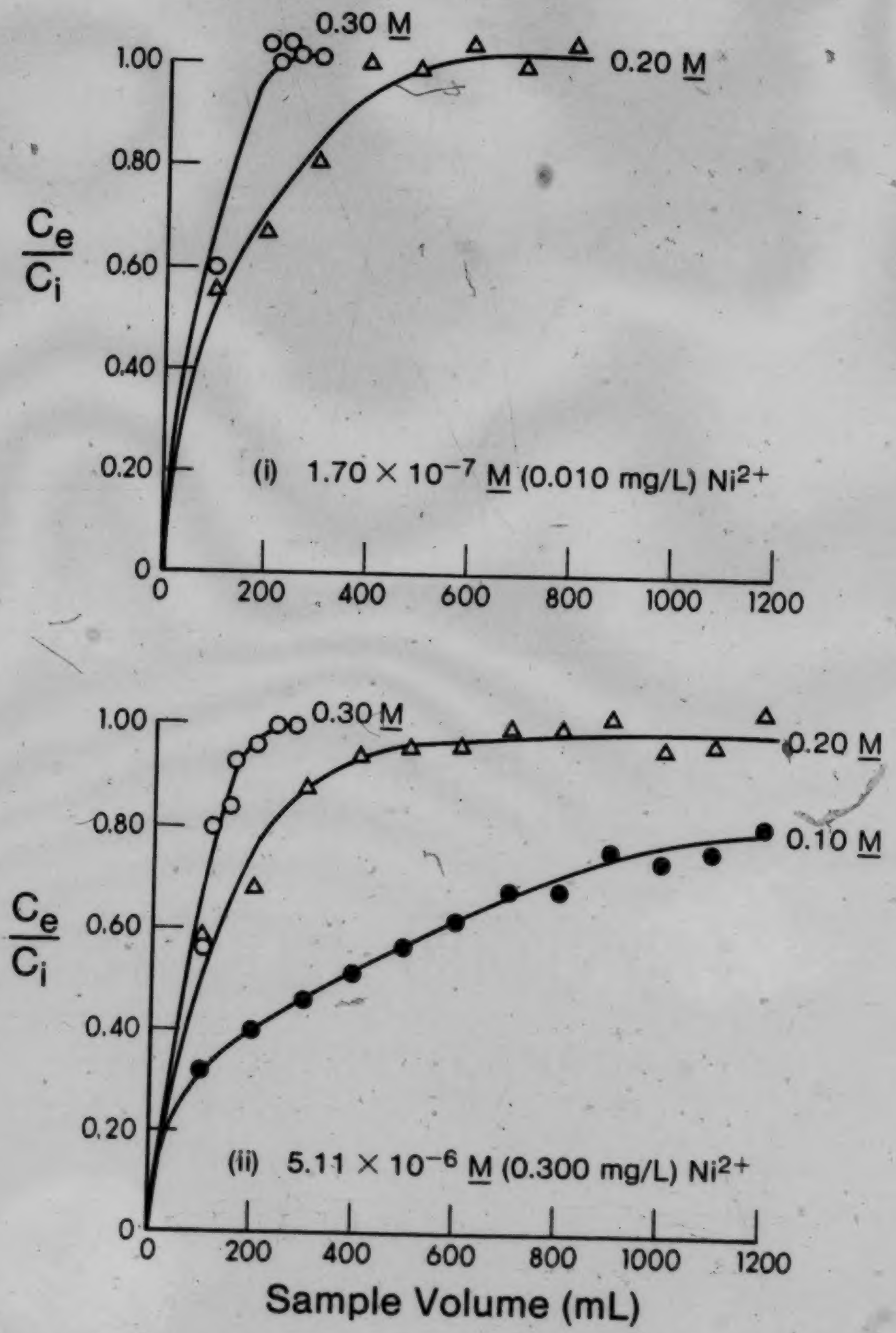


Figure 6.5 Breakthrough Curves for Nickel Standard Solutions at Various Ionic Strengths (Flow Through Method)

All subsequent column experiments were conducted using solutions adjusted to 0.20 M $NaNO_3$.

2. Eluting Acid

Elution profiles for Ni^{2+} sorbed on 0.300 g resin were measured using 1.0, 2.0 and 4.0 M HNO_3 as eluant (Figure 6.6).

Quantitative elution was achieved with 40 mL of either 2.0 or 4.0 M HNO_3 and with 70 mL of 1.0 M acid. In subsequent studies, 50.0 mL of 2.0 M HNO_3 was used for elution.

An experiment was carried out to determine whether the glass wool used to support resin in the columns affected analytical results. One litre volumes of blank solutions (0.20 M $NaNO_3$) were passed through two columns containing 0.300 g resin retained by a plug of glass wool and 1 L aliquots of 8.52×10^{-7} M (0.050 mg/L) Ni^{2+} in 0.20 M $NaNO_3$ were passed through two columns containing only glass wool plugs. All columns were eluted with 50.0 mL of 2 M HNO_3.

Table 6.5 shows GFAAS absorbance values measured for the four acid eluates. The absorbance values were the same for all four samples showing that the glass wool neither removed nickel from sample solutions nor contributed nickel to acid eluates.

3. Summary of Experimental Conditions

The experimental conditions used for the flow through column method were:

Sample volume (mL) = 1000

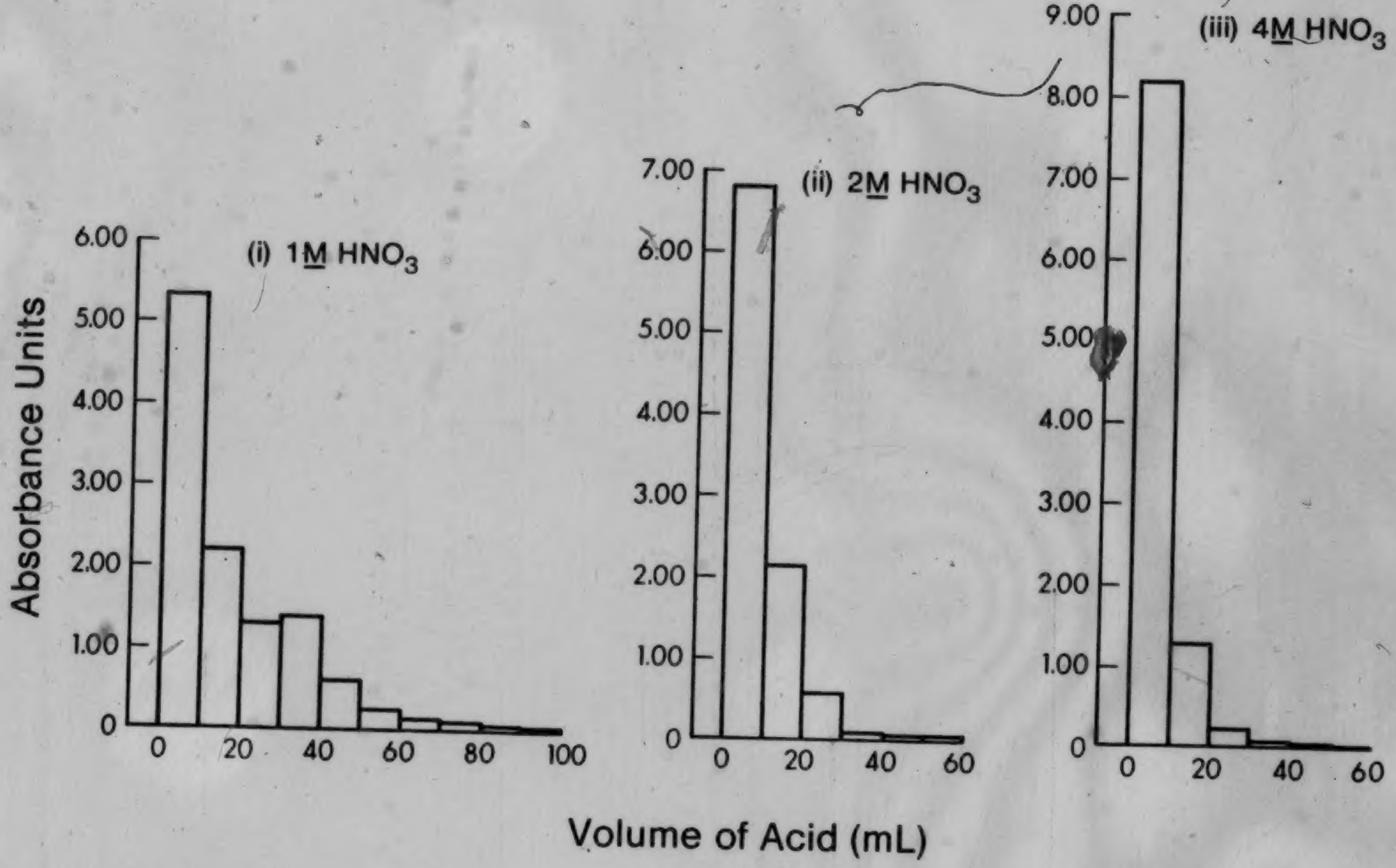


Figure 6.6 Elution Profiles Using Varying Concentrations of HNO$_3$ (Flow Through Method)

Table 6.5 Effect of Glass Wool Plug in Columns (Flow Through Method)

Column	1	2	3	4
Resin (g)	0.300	0.300	None	None
Sample	Blank	Blank	Ni^{2+}	Ni^{2+}
Absorbance	0.024	0.023	0.023	0.021

Weight of resin (g) = 0.300

μ (M) = 0.20

Volume (mL)/concentration (M)
of eluting acid = 50.0/2.0

6.3.2.2 Measurement of λ_o

Two experiments were carried out to accurately determine λ_o. Each involved the passage of replicate 8.52×10^{-7} M (0.050 mg/L) standard nickel solutions through resin columns. One experiment was carried out at pH 8.0_0 and the other was at pH 7.0_0. The experiments were carried out at two pH values to check whether OH^- and CO_3^{2-} complexes of nickel were formed at pH 8.0_0.

The results for these experiments are tabulated in Table 6.6. The data at pH 8.0_0 include results from two batches of resin; one was prepared prior to starting development of the batch method and the other was prepared prior to using the flow through method for analysis of sewage samples (Section 7.4). Although λ_o values carried out at pH 7.0_0 were a little lower than those at pH 8.0_0, the pH 7.0_0 values agreed with those at pH 8.0_0 at the 95% confidence level. These results suggest that OH^- and CO_3^{2-} nickel complexes can be ignored. The pooled average of λ_o for all the data in Table 6.6 was 0.53 ± 0.03 L/g.

The minimum detectable concentration (MDC) of Ni^{2+}, using 20 μL injection volumes to the AAS furnace, was estimated by passing twelve 1 L aliquots of blank solution

Table 6.6 Means and Standard Deviations for Replicate λ_o Values (Flow Through Method)

pH	n	λ_o (L/g)
8.0	20	0.54 ± 0.03
7.0	4	0.48 ± 0.01

(i.e. 0.20 M $NaNO_3$) buffered at pH 8.0_0 through twelve resin columns and analyzing each for Ni^{2+} in the usual manner. The spectrophotometer was zeroed on the empty furnace. Concentrations ranged from 1.29×10^{-8} to 2.14×10^{-8} M (0.0008 - 0.0010 mg/L) with mean and standard deviation values of $(1.80 \pm 0.21) \times 10^{-8}$ M. The MDC was taken to be twice the standard deviation and had a value of 4×10^{-9} M or 0.0003 mg/L. An identical value was obtained when eluate from one of the twelve columns was injected 36 times, suggesting that the scatter in blank absorbance values is associated with instrumental "noise" rather than with variation in the nickel eluted from blank resin columns.

6.3.2.3 Measurement of [Ni^{2+}] in Synthetic Solutions

Three experiments were conducted to measure [Ni^{2+}] in synthetic solutions using EDTA and gly-ala as model ligands. These experiments were conducted at the following pH, total nickel and total ligand concentrations.

Experiment	1	2	3
Ligand	EDTA	EDTA	gly-ala
Total Ni conc.	1.70×10^{-6} M	1.70×10^{-7} M	1.70×10^{-6} M
Total ligand conc.	8.52×10^{-7} M	8.52×10^{-8} M	1.00×10^{-3} M
pH	7.0_0	7.0_0	8.0_0

Both EDTA solutions were unbuffered with respect to free nickel whereas the gly-ala solution was well buffered in free nickel.

The mean ± 1 standard deviation values for these data are compared with calculated Ni^{2+} concentrations in Table 6.7. In calculating the fractions of nickel present in various forms at $\mu = 0.20$ M and pH = 8.0_0 ($\alpha_{Ni} = 0.087 \pm 0.03$, $\alpha_{NiL^+} = 0.290 \pm 0.10$) starting with equilibrium constants given for $\mu = 0.10$ M (Martell and Smith, 1974), single-ion activity coefficients were calculated with the extended Debye-Hückel equation assuming an ionic size parameter of 3 x 10^{-8} cm for all ions (Laitinen and Harris, 1975). Further refinement of these calculations seemed unjustified in view of the large errors in β_1 and β_2 given by Sychev and Mitsul (1967).

The mean $[Ni^{2+}]$ measured in the first experiment with EDTA as the ligand (8.55 x 10^{-7} M) was in excellent agreement with the calculated concentration of 8.48 x 10^{-7} M. Agreement between the measured and calculated Ni^{2+} concentrations for a ten-fold lower concentration was still quite acceptible (calculated pNi = 7.07, measured pNi = 6.92) considering the low concentration and the potential systematic errors resulting from adsorption of nickel or EDTA onto glassware.

The calculated and measured $[Ni^{2+}]$ for the gly-ala solution agreed within ± 2 standard deviations.

It is interesting, in comparing these gly-ala results with those from the batch method, that the measured $[Ni^{2+}]$ was slightly more than twice as large as the calculated $[Ni^{2+}]$ in both cases. This may reflect a systematic error

Table 6.7 Summary of Data for Synthetic Solutions (Flow Through Method)

Experiment	n	Ligand	Calculated[Ni^{2+}] ($\underline{M}$, x 10^{7})	Measured[Ni^{2+}] ($\underline{M}$, x 10^{7})
1	3	EDTA	8.48	8.5 ± 0.2
2	4	EDTA	0.85	1.2 ± 0.4
3	10	gly-ala	1.4 ± 0.5	2.9 ± 0.3

in the values used for the formation constants. Although the authors reporting these values indicate an uncertainty of only 9% (Sychev and Mitsul, 1967), which is the uncertainty used in estimating the error in the calculated $[Ni^{2+}]$, Martell and Smith (1974) consider the β_2 value to be "questionable". The close agreement of the ratio of measured and calculated $[Ni^{2+}]$ obtained by the flow through method at $\mu = 0.20$ M with the same ratio obtained by the batch method at $\mu = 0.10$ M suggests that uptake of the species NiL^+ is negligible. If it were not, then uptake of NiL^+ would have produced a higher ratio at $\mu = 0.20$ M.

7. MEASUREMENT OF FREE NICKEL ION CONCENTRATIONS IN SEWAGE

The results of measuring free nickel ion concentrations, [Ni^{2+}], in Edmonton sewage samples using the batch and flow through column methods are presented in this chapter. Free nickel ion concentrations were measured to determine their magnitudes in sewage as well as for the determination of complexation capacities. Sewage samples were centrifuged prior to analysis for [Ni^{2+}] to prevent suspended material from clogging the resin. The results from a study to assess suitable centrifugation rates are also presented.

7.1 SEWAGE COLLECTION

Grab samples of raw sewage and primary effluent were collected from the positions shown in Figure 7.1.

7.2 EVALUATION OF SAMPLE CENTRIFUGATION RATES

The previous use of filtration through 0.45 μm membrane filters in this research program showed that filtered nickel results were particularly prone to severe contamination even though filters were carefully acid washed (refer Section 5.2.3). Sample centrifugation was investigated as a means of removing particulate matter. Aliquots of the same sample were centrifuged at various speeds (1600 x g to 48 300 x g) for 15 min and analyzed for total copper and nickel after

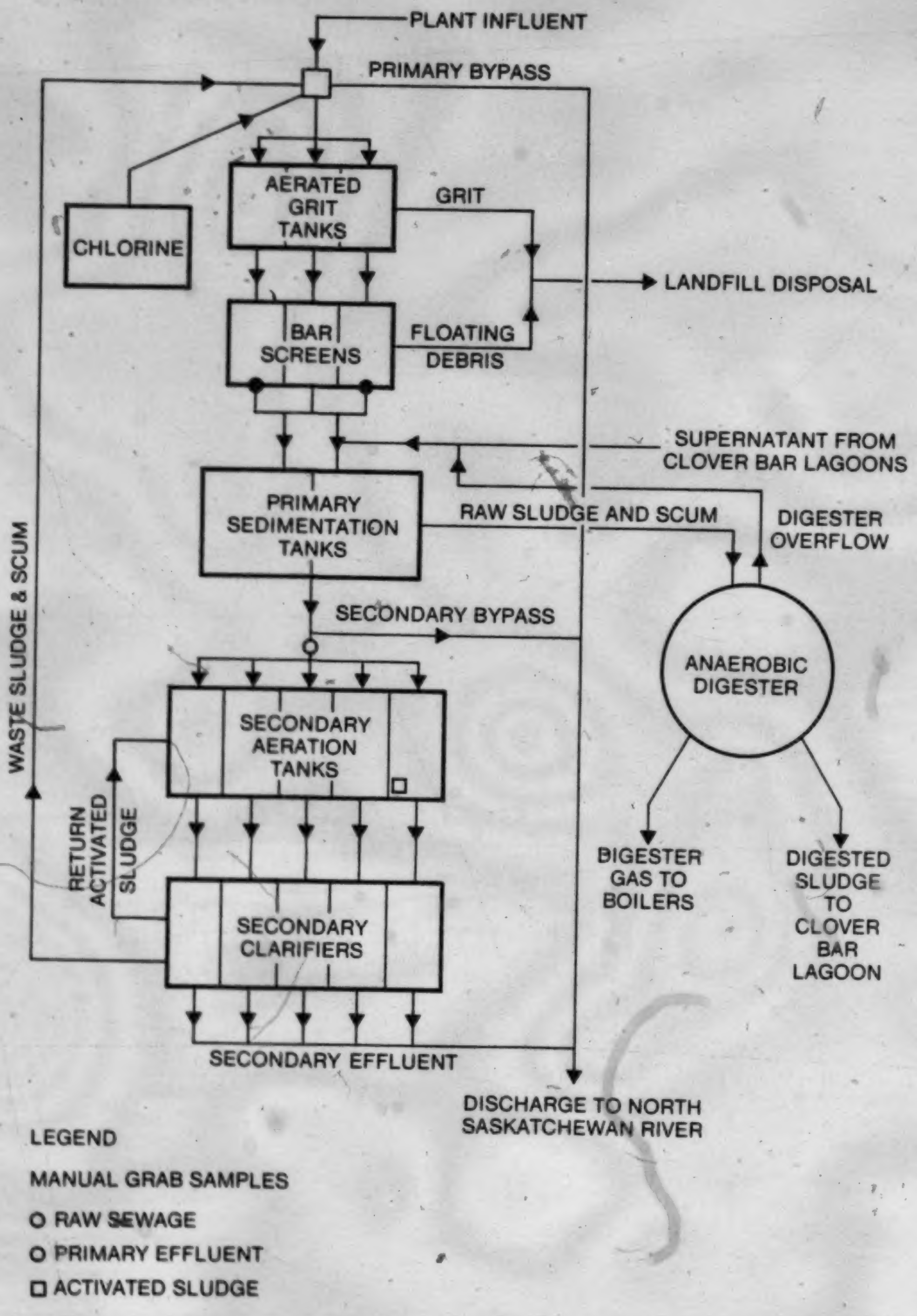

PLANT INFLUENT
PRIMARY BYPASS
CHLORINE
AERATED GRIT TANKS
GRIT
LANDFILL DISPOSAL
BAR SCREENS
FLOATING DEBRIS
SUPERNATANT FROM CLOVER BAR LAGOONS
PRIMARY SEDIMENTATION TANKS
RAW SLUDGE AND SCUM
DIGESTER OVERFLOW
SECONDARY BYPASS
ANAEROBIC DIGESTER
WASTE SLUDGE & SCUM
SECONDARY AERATION TANKS
RETURN ACTIVATED SLUDGE
SECONDARY CLARIFIERS
DIGESTER GAS TO BOILERS
DIGESTED SLUDGE TO CLOVER BAR LAGOON
SECONDARY EFFLUENT
DISCHARGE TO NORTH SASKATCHEWAN RIVER
LEGEND
MANUAL GRAB SAMPLES
○ RAW SEWAGE
○ PRIMARY EFFLUENT
□ ACTIVATED SLUDGE

Figure 7.1 Sampling Sites for Studies Involving Free Nickel Ion Determinations

pressure digestion. Table 7.1 shows the results for copper and nickel from three samples.

These results show that, in contrast to copper, nickel exists predominantly in the soluble phase (as operationally defined by speed of centrifugation). The centrifugation speed only had a slight effect on nickel concentrations. Copper concentrations, on the other hand, were greatly affected by the speed of centrifugation and even centrifugation at 48 300 x g did not remove as much particulate matter as filtration through 0.45 μm membrane filters.

Samples were consequently centrifuged at 12 000 to 13 000 x g for 15 min prior to analysis for $[Ni^{2+}]$.

7.3 USE OF THE BATCH METHOD

7.3.1 Measurement of $[Ni^{2+}]$

Samples were centrifuged and $NaNO_3$ was added to a final concentration of 0.10 M. The pH of blanks and samples were adjusted to the initial pH of the particular sample with CO_2 and NaOH. Blank (i.e. 0.10 M $NaNO_3$) and sample aliquots of 50.0 mL were then shaken with several weights of resin as described in Section 6.3.1. Supernatants were acidified and digested before analysis for total soluble nickel.

Table 7.2 shows GFAAS absorbance values measured in the supernatants of sewage samples equilibrated with various

Table 7.1 Nickel Results from Centrifugation and Filtration Studies

Sample (Date)[1]	Treatment[2]	Concentration (mg/L)	
		Cu	Ni
Raw sewage (21-7-81)	None	0.040	0.018
	b	0.006	0.011
	c	0.004	0.011
Primary effluent (7-4-81)	None	0.031	0.029
	a	0.008	0.025
	b	0.008	0.023
	Filtration[3]	0.002	contam.[4]
Primary effluent (16-4-81)	b		0.022
	c		0.022

[1] Date of sample collection

[2] Letters refer to centrifugation speeds as follows:
a. 3200 r.p.m. (1600 x g)
b. 5000 r.p.m. (12 075 x g)
c. 20 000 r.p.m. (48 300 x g)

[3] Filtration through 0.45 μm

[4] Contamination

weights of resin. There seems little doubt that the nickel signal was enhanced as the weight of resin was increased. This positive interference was large and absorbances measured in the samples after equilibration with resin were larger than those measured before contact with resin. The low blank absorbance values showed that the interference was not caused by nickel being released from the resin during the equilibration period.

Aliquots of the raw sewage and primary effluent samples (Experiment 2, Table 7.2) were also used to check for the presence of interferences (Section 7.3.2).

7.3.2 Interference Studies

Possible interferences in GFAAS have been summarized in Section 4.3.3.

The presence of background absorption was tested by analyzing a blank sample (i.e. 0.10 $\underline{M}$ $NaNO_3$ + 1% (by volume) HNO_3), a standard nickel solution (0.020 mg/L in 0.10 $\underline{M}$ $NaNO_3$ + 1% HNO_3) and an aliquot of the acidified raw sewage supernatant used previously. These samples were analyzed twice as follows: (i) the deuterium background (BG) lamp at the nickel absorbing wavelength (232.0 nm) was used to detect whether broad-band absorption was occurring; and, (ii) the nickel source together with the deuterium lamp (AA-BG) was used at a nickel non-absorbing wavelength (229.2 nm) to determine whether the deuterium lamp was providing adequate correction for any background absorption.

Table 7.2 Nickel Absorbance Values for Sewage Samples Equilibrated with Various Weights of Resin (Batch Method)

Experiment	Sample	Resin (g)	Absorbance
1	Blank	0.500	0.001
	Primary effluent	0	0.024
		0.200	0.029
		0.500	0.039
		1.000	0.059
		1.500	0.088
		2.000	0.103
2	Blank	0.500	0.001
	Raw sewage	0	0.066
		0.200	0.085
		0.500	0.111
		1.000	0.160
	Primary effluent	0	0.079
		0.200	0.110
		0.500	0.172
		1.000	0.238

The measurement of zero absorbances demonstrate that background absorption is being compensated for by the deuterium lamp.

Table 7.3 shows GFAAS absorbance values using the wavelengths and lamps described. Background absorption occurred for all the samples. The fact that it also occurred for the blank and Ni standard solutions suggests that it was not caused by organic matter but by sodium nitrate. The background absorption was, however, well compensated for by the deuterium background corrector.

In order to determine whether the positive interference could be overcome by the method of standard additions, standard nickel spikes were added to sewage samples which had not been contacted with resin, and samples which had been equilibrated with various weights of resin. The samples used were the same as for the second experiment presented in Table 7.2.

Table 7.4 presents nickel recoveries obtained for this experiment. It is evident that quantitative recoveries were achieved for samples which had not been equilibrated with resin and that incomplete nickel recoveries occurred in samples after resin equilibration. Furthermore, there was some indication that the extent of this interference increased as the weight of resin increased. These results showed that the added nickel behaved in the opposite manner to the apparent original nickel (which appeared to increase as the weight of resin increased). The method of standard

Table 7.3 Results Obtained to Determine the Presence of Background Absorption (Batch Method)

Sample(1)	Wavelength (nm)	Lamp(s)	Absorbance
a	232.0	BG	1.19
b	232.0	BG	1.26
c	232.0	BG	0.958
a	229.2	AA-BG	0.000
b	229.2	AA-BG	0.000
c	229.2	AA-BG	0.001

(1)Samples are: a. 0.10 M $NaNO_3$ + HNO_3 (1% by volume)

b. 0.020 mg/L Ni prepared in 0.10 M $NaNO_3$ + HNO_3 (1% by volume)

c. Raw sewage supernatant + 0.10 M $NaNO_3$ + HNO_3 (1% by volume)

Table 7.4 Nickel Recoveries from Spiked Sewage Samples Before and After Equilibration with Resin (Batch Method)

Sample	Standard Addition	Resin	Recovery (mg/L)	
	(mg/L)	(g)	Before equil.	After equil.
Raw sewage	0.010	0	0.011	
		0.200		0.008
		0.500		0.004
		1.000		0.007
	0.020	0	0.018	
		0.200		0.012
		0.500		
		1.000		0.009
Primary effluent	0.010	0	0.010	
		0.200		0.006
		0.500		0.008
		1.000		0.004
	0.020	0	0.019	
		0.200		0.015
		0.500		0.015
		1.000		0.010

additions was not applicable to overcoming the positive interference measured in samples equilibrated with resin.

In the final experiment to elucidate the interference, excess EDTA (0.02 M) was added to centrifuged raw sewage samples which had and which had not been equilibrated with resin. These samples were not acidified prior to analysis for nickel and 0.02 M EDTA solutions in water were used as the GFAAS blanks. The purpose of this experiment was to determine whether EDTA would complex the constituent(s) causing the positive interference, thereby eliminating it. The experiment was also run in duplicate using aliquots of the same samples acidified with HNO_3 (1% by volume) instead of adding EDTA.

Table 7.5 shows absorbance values for the samples used. Absorbance values for the samples with EDTA were higher than for the corresponding acidified samples. The presence of chlorides, nitrates and sulphates have been demonstrated many times to suppress GFAAS signals for various metals (Czobik and Matousek, 1978; Guevremont, 1980; Hageman *et al.*, 1979), and EDTA has been effectively used to eliminate this type of matrix interference (Guevremont, 1980; Matsusaki *et al.*, 1979). Sample absorbances also increased in the presence of EDTA as the weight of resin was increased, although to a lesser extent than in the acidified samples.

In summary, the enhancement of nickel signals observed when sewage samples were equilibrated with resin in the

Table 7.5 Nickel Absorbance Values for Raw Sewage Samples to which HNO_3 and EDTA Were Added (Batch Method)

Sample	Resin (g)	Absorbance	
		HNO_3	EDTA
Before equilibration	0	0.330	0.414
After equilibration	0.300	0.378	0.450
	1.000	0.426	0.462

batch mode was symptomatic of spectral or matrix interferences. It could not be prevented by using the method of standard additions or by modifying the matrix by the addition of excess EDTA. Sorption of L-containing species, such as HL, onto the resin (refer Assumption 4, Section 6.1.2) can cause the value of λ to increase as the weight of resin is increased, with a possible increase in $T_{M,S}/V$ (refer equations in Section 6.1). However, this effect cannot cause $T_{M,S}/V$ to be greater than T_M/V, as was observed (refer Table 7.2). These conclusions invalidated the use of the batch method for measuring $[Ni^{2+}]$ in Edmonton sewage and prompted the use of the flow through method.

7.4 USE OF THE FLOW THROUGH COLUMN METHOD

Partway through the sewage work it was necessary to prepare a new batch of resin. It was also felt that the use of 1 L samples for the flow through method would require the centrifugation of prohibitively large volumes of sewage for the determination of complexation capacities. The new resin and the effect of scaling the flow through method described in Section 6.2.3 down by 50% were tested by using 500 mL sample volumes, resin weights of 0.100 g and 20.0_0 mL acid eluant volumes. Replicate standard nickel solutions of 8.52×10^{-7} $\underline{M}$ (0.050 mg/L) at pH 8.0_0 were used to measure λ_o values using these "scaled down" conditions. The mean and standard deviation for λ_o using 8 replicates was

0.53 ± 0.03 L/g, which was identical with the value of 0.54 ± 0.03 L/g previously obtained with 1 L sample volumes and 0.300 g resin (refer Section 6.3.2.2).

Hence 1 L or 500 mL centrifuged sample aliquots, buffered at the original sample pH with CO_2 and NaOH, and containing 0.20 M $NaNO_3$, were passed through columns containing 0.300 g or 0.100 g weights of resin respectively. The resin was eluted with 50.0 or 20.0_0 mL HNO_3 respectively, and analyzed for nickel as described in Section 6.3.2.1.

Organic matter is known to irreversibly foul ion exchangers causing losses in ion exchange capacity (Kunin, 1963). In order to demonstrate that no organic fouling of the resin occurred during the passage of centrifuged sewage, three different volumes of the same centrifuged and spiked raw sewage sample were passed through three columns containing the same weights of resin. Samples were spiked with 4.26×10^{-6} M (0.250 mg/L) Ni, resin weights of 0.100 g were used and the sample aliquots used were 500, 1000 and 1500 mL.

Table 7.6 shows the results for this experiment. The mean and standard deviation values obtained for $[Ni^{2+}]$ were $(6.1 \pm 0.25) \times 10^{-7}$ M and no trend was observed with increasing volume of sewage.

Table 7.6 Results from Passing Various Sample Volumes Through 0.100 g Weights of Resin (Flow Through Method)

Volume (mL)	$[Ni^{2+}]$	
	$\underline{M}, \times 10^{7}$	mg/L
500	6.2	0.036
	6.1	0.036
1000	6.4	0.038
	5.8	0.034
1500	5.8	0.034
	6.2	0.036

7.4.1 Measurement of $[Ni^{2+}]$

Table 7.7 presents total and free nickel ion concentrations measured in grab samples of Edmonton sewage collected during late 1981 and early 1982.

Nine of the samples contained no free nickel (i.e. < $4x10^{-9}$ M) and in the other samples, $[Ni^{2+}]$ represented 6% or less of the total soluble (i.e. centrifuged) nickel. Evidently nickel was strongly complexed in these samples, suggesting that Edmonton sewage contains a high concentration of ligand(s) and/or very strong ligand(s). In contrast to the uniformly negligible $[Ni^{2+}]$ in these samples, considerable variation was evident for the total nickel concentrations in both the uncentrifuged and centrifuged samples. These total nickel results also confirm the conclusion drawn from Table 7.1 that nickel exists predominantly in the soluble phase. Indeed, in one of the samples collected (19-2-82), all of the nickel appeared to be soluble.

7.4.2 Measurement of Complexation Capacities

Titration experiments were performed to determine complexation capacities of Edmonton raw sewage in order to answer the question of how much nickel the sewage could complex before $[Ni^{2+}]$ became appreciable.

Centrifuged raw sewage samples were adjusted to 0.20 M $NaNO_3$, buffered to their own initial pH values with CO_2 and NaOH and each was divided into six to ten 500 mL or 1 L

Table 7.7 Total and Free Nickel Concentrations in Edmonton Raw Sewage

Date	pH	$C_{Ni}^{(1)}$ $\underline{M}$, x 10^7 (mg/L) Uncentrifuged	$C_{Ni}^{(1)}$ $\underline{M}$, x 10^7 (mg/L) Centrifuged	$[Ni^{2+}]^{(2)}$ $\underline{M}$, x 10^9 (mg/L) Centrifuged
20-11-81	7.35	12 (0.070)	7.7 (0.045)	N.D.(3)
21-11-81	8.10	8.2 (0.048)	4.4 (0.026)	N.D.
23-11-81	7.90	5.3 (0.031)	3.2 (0.019)	5.1 (0.0003)
23-11-81	7.70	7.7 (0.045)	3.8 (0.022)	N.D.
24-11-81	8.90	11 (0.064)	5.6 (0.033)	N.D.
1-12-81	7.85	9.9 (0.058)	5.1 (0.030)	16 (0.001)
2-12-81	8.20	7.0 (0.041)	3.6 (0.021)	N.D.
16-12-81	8.25	7.5 (0.044)	4.8 (0.028)	N.D.
18-12-81	8.20	7.8 (0.046)	4.9 (0.029)	N.D.
9-2-82	7.90	11 (0.062)	5.8 (0.034)	29 (0.002)
19-2-82	8.00	15 (0.088)	15 (0.088)	N.D.

(1) C_{Ni} is total nickel concentration in centrifuged samples

(2) $[Ni^{2+}]$ is free nickel ion concentration

(3) N.D. is not detected, i.e. < 4 x 10^{-9} $\underline{M}$

aliquots. Nickel was added in increasing amounts to all but one of the aliquots and each was analyzed for [Ni^{2+}]. The aliquot with no nickel added was analyzed for both [Ni^{2+}] and total soluble nickel. This aliquot was also used for the determination of total organic carbon, TOC, and nitrilotriacetic acid, NTA.

The results of these titrations are shown in Figures 7.2 to 7.7 as plots of [Ni^{2+}] versus total nickel concentrations. Figure 7.6 is for primary effluent and the other plots are for raw sewage samples.

The intersection point of the rising part of the curve with the horizontal axis was taken to be the complexation capacity in each case. It is evident that these sewage samples contained appreciable excess complexing capacity for nickel. The sharpness of the intersection points suggests that the major ligand(s) in the sewage form very stable complexes with nickel.

The slopes of the rising part of the titration plots do not approach unity, as expected for plots of [Ni^{2+}] versus total nickel when the complexation capacity has been completely exceeded (Bhat *et al.*, 1981). This can be explained by the presence of large concentrations of ligands which form very weak complexes with nickel. Presumably the slopes of the lines in these plots would be unity when the complexation capacity of these very weak ligands has been exceeded. As a result, the complexation capacities measured on Edmonton sewage are perhaps better described as "strong

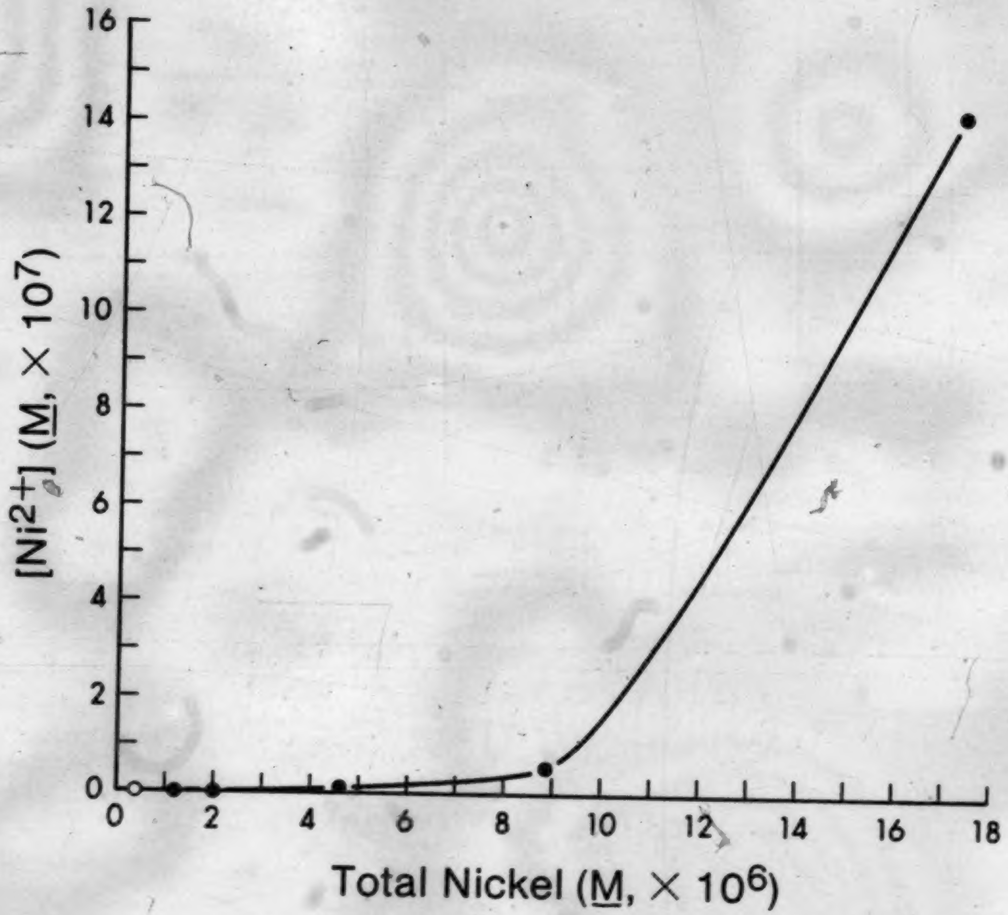


Figure 7.2 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (2-12-81)

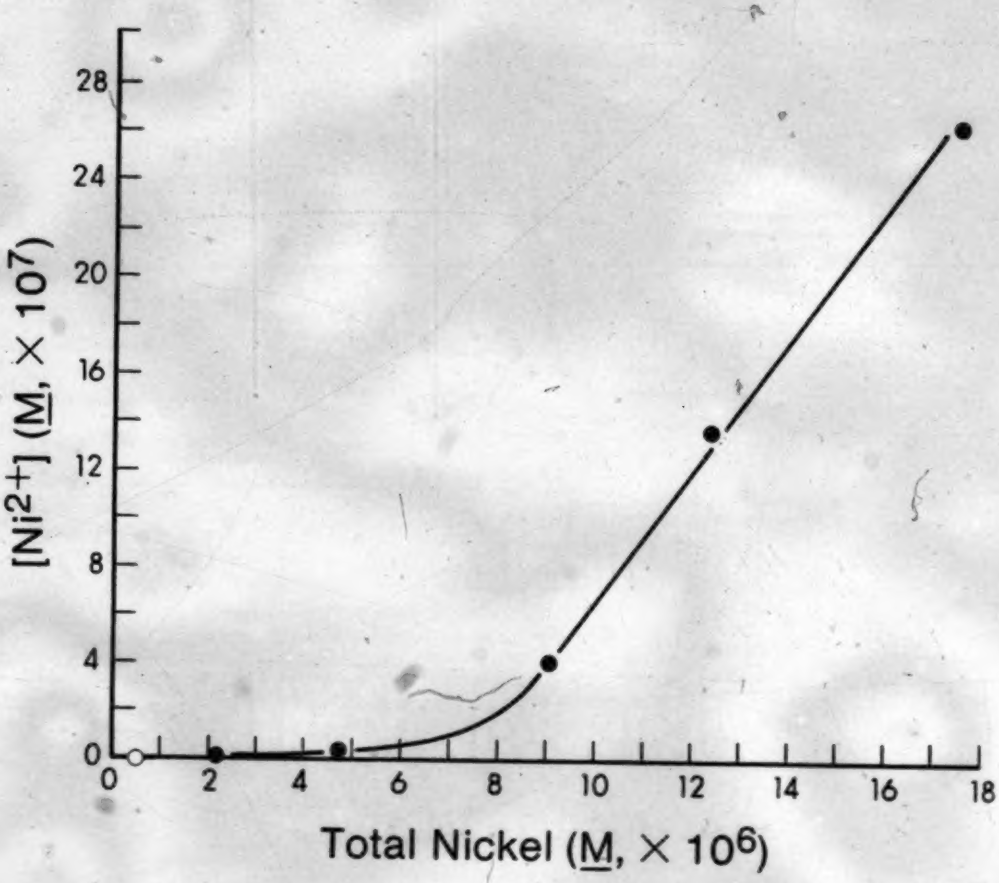


Figure 7.3 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (16-12-81)

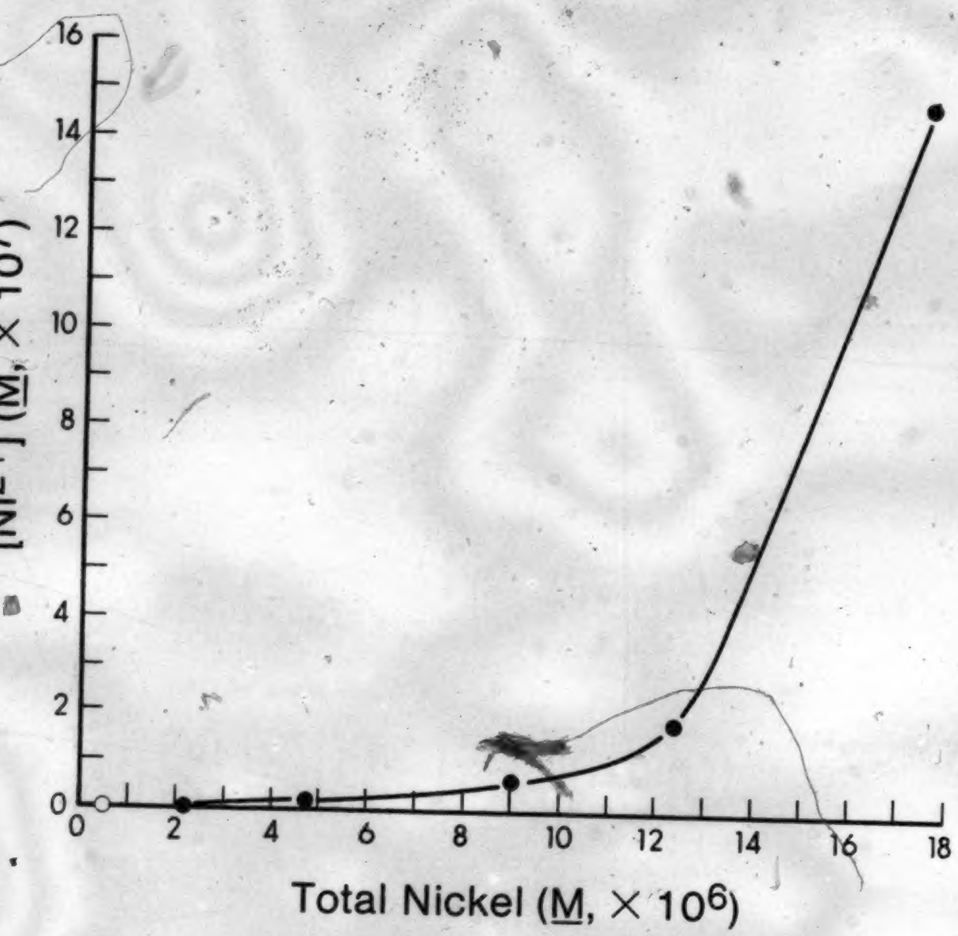


Figure 7.4 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (18-12-81)

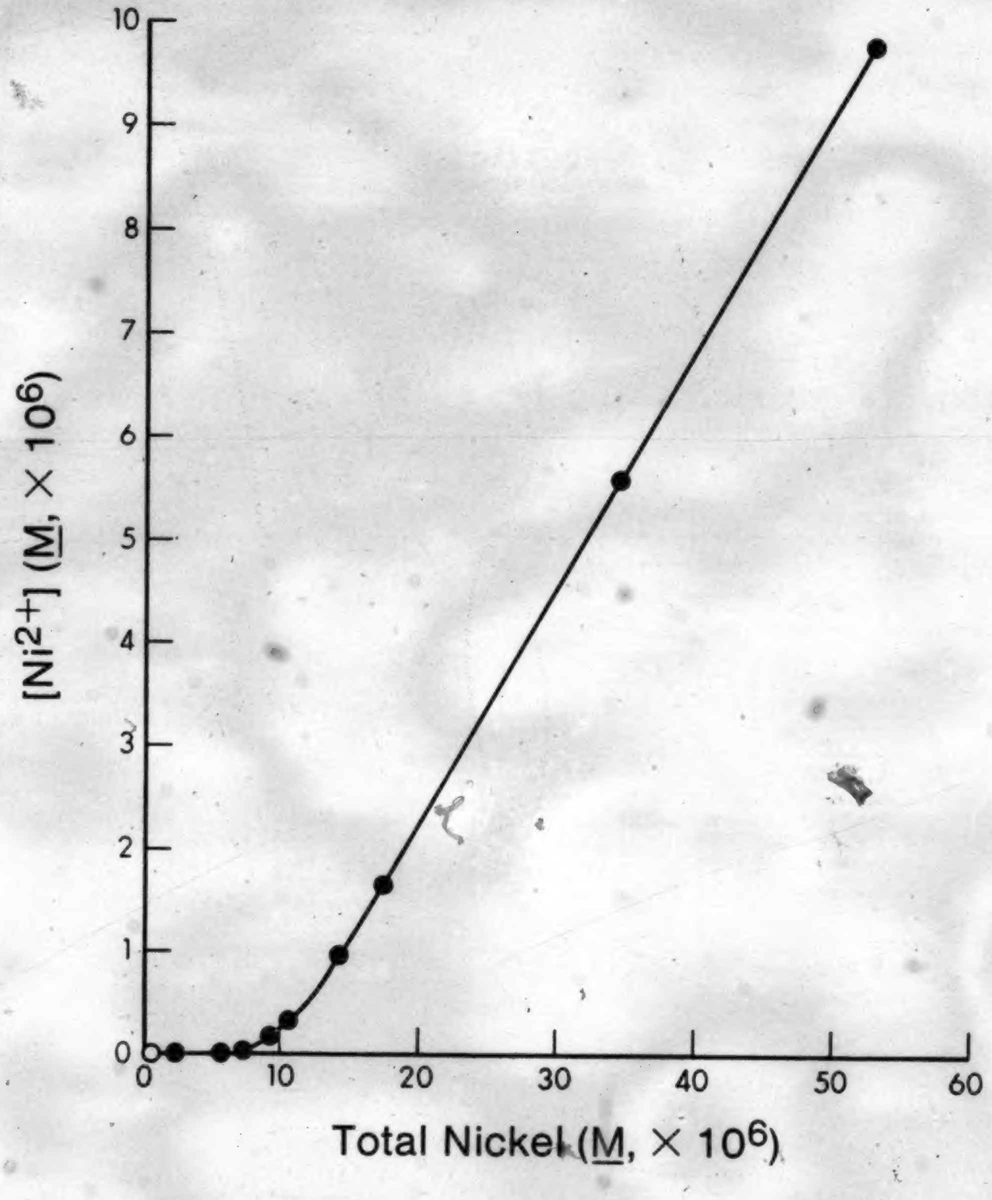


Figure 7.5 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (9-2-82)

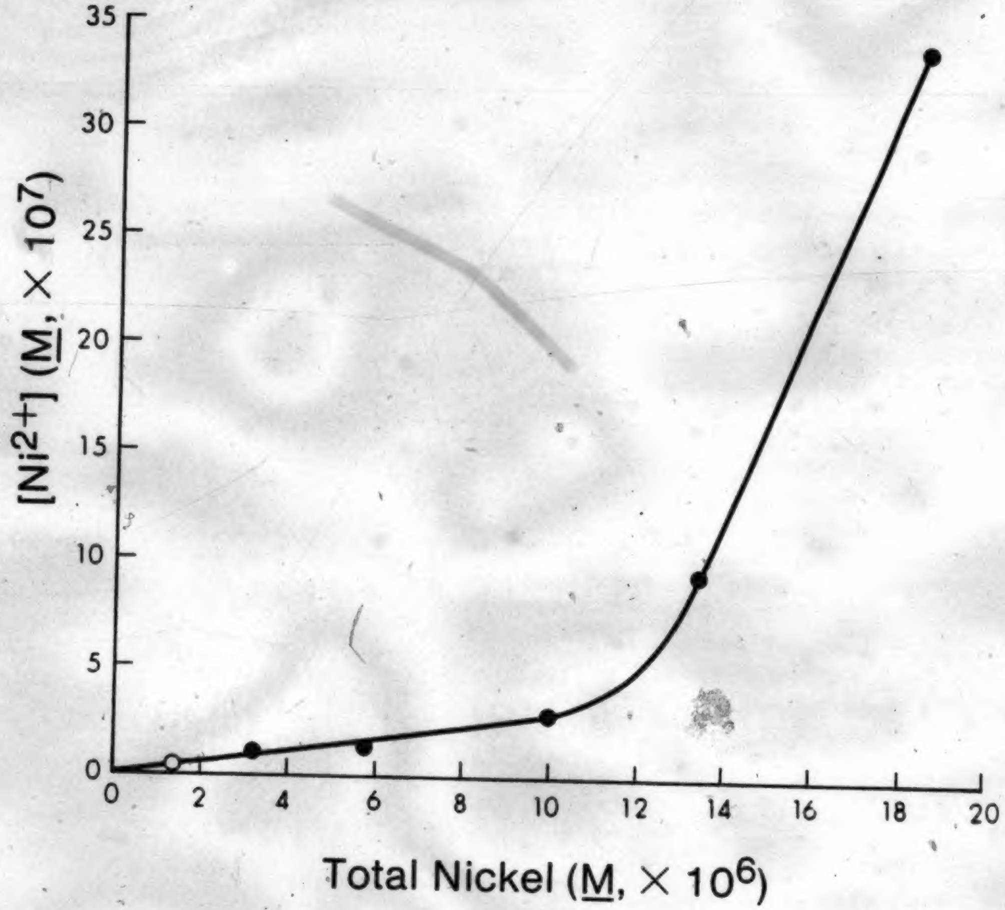


Figure 7.6 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (19-2-82)

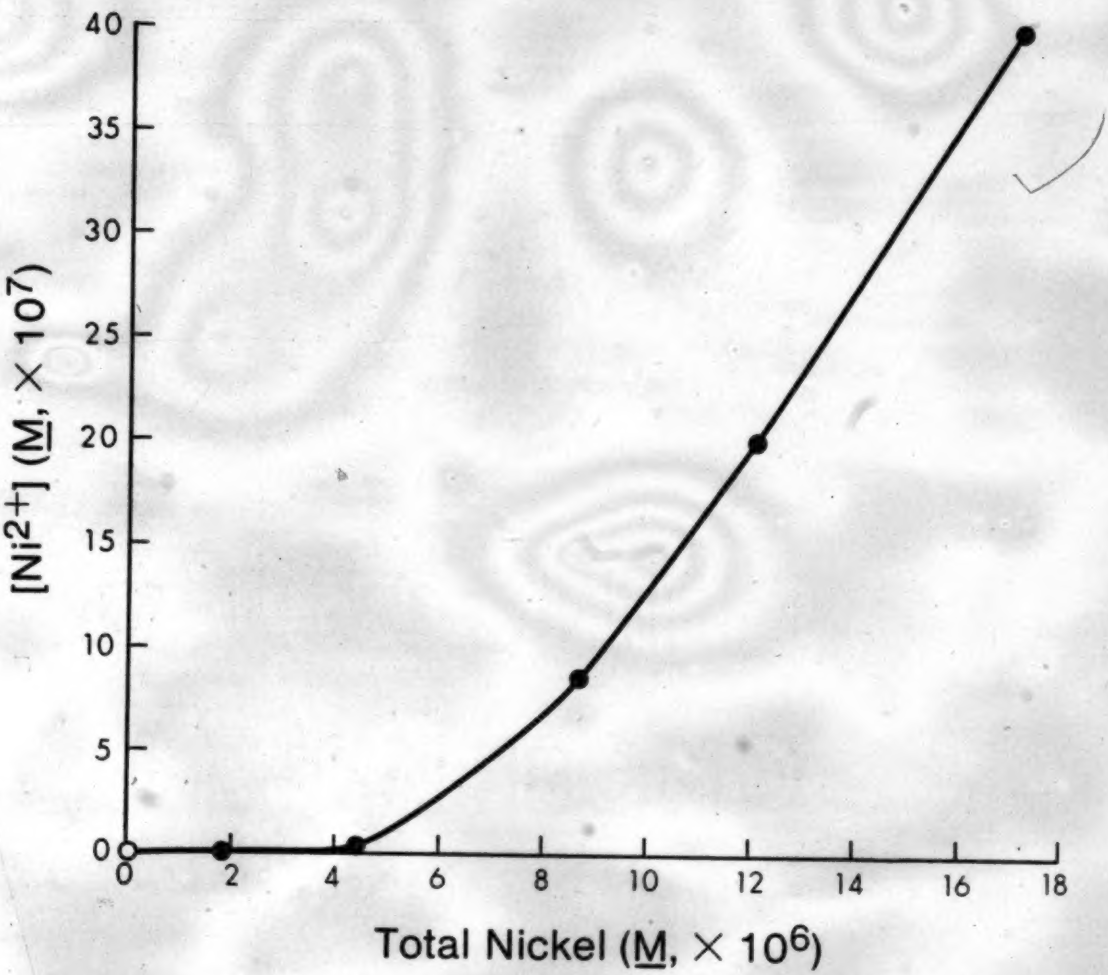


Figure 7.7 Titration of Sewage with Nickel(II). The open circle is before addition of nickel (1-3-82)

complexation capacities".

Table 7.8 summarizes the complexation capacities from Figures 7.2 to 7.7 together with NTA and TOC results.

The complexation capacity results were surprisingly constant; the mean ±1 standard deviation for these data was $(9.6 \pm 1.9) \times 10^{-6}$ $\underline{M}$. Hence total soluble nickel concentrations larger than about 1×10^{-5} $\underline{M}$ (0.6 mg/L) were required for $[Ni^{2+}]$ to become appreciable. These complexation capacity values fall in the range of 1×10^{-6} to 8×10^{-5} $\underline{M}$ previously found in secondary sewage effluents using ASV and copper as the titrant (Bender *et al.*, 1970). City of Chicago domestic sewage supplemented with brewery effluent was found to have complexation capacities of about 10^{-6} $\underline{M}$ using an ion exchange method with copper and nickel as titrants (Beers, 1979; Hickey, 1979).

The TOC concentrations were not correlated with the complexation capacity values. These data indicate that gross measures of organic matter, such as TOC, are inappropriate as a measure of nickel-complexing ligands.

Concentrations of NTA were a little larger (≤ 3 times) than the corresponding complexation capacities. Nickel is capable of forming NiL^- and NiL_2^{4-} species with NTA. Calculations using published pKa and stability constants at 25°C and 0.1 μ ($pKa_1 = 0.8$, $pKa_2 = 1.8$, $pKa_3 = 2.48$; $pKa_4 = 9.65$, $\log \beta_1 = 11.50$ and $\log \beta_2 = 16.32$ (Martell and Smith, 1974)), a total NTA concentration of 10^{-5} $\underline{M}$ and a pH of 8.0_0, showed that nickel is almost entirely complexed as the

Table 7.8 Summary of "Strong Complexation Capacity", TOC and NTA Results

Date	Complexation Capacity $\underline{M}$,x10^6	NTA $\underline{M}$,x10^5	TOC mg/L
2-12-81	9.6	1.3	132
16-12-81	7.8	2.7	84.5
18-12-81	12	3.5	80.0
9-02-82	10		142
19-02-82	11	2.6	34.9
1-03-82	7.0		

$(Ni\text{-}NTA)^-$ species ($\alpha_{NiL^-} = 0.99$, $\alpha_{NiL_2^{4-}} = 0.01$). Consequently, the formation of NiL_2^{4-} complexes with NTA cannot be used to explain why measured NTA concentrations are larger than the corresponding complexation capacities.

Possible explanations for this discrepancy include inaccuracies in the polarographic method used to determine NTA; and, a decrease in measured complexing capacity caused by biological degradation of NTA during the time required for each determination of the complexation capacity. Samples for NTA determinations were acidified immediately after centrifugation, whereas complexation capacity determinations lasted several hours. Nitrilotriacetic acid has been shown to be biologically degraded in activated sludge treatment plants (Bouveng *et al.*, 1968; Stoveland *et al.*, 1979c) and in natural waters (Chau and Shiomi, 1972). It appears, however, that NTA may be a major ligand for nickel complexation reactions in Edmonton sewage.

Total (calcium + magnesium) concentrations in Edmonton sewage are probably about 10^{-3} $\underline{M}$ (based on potable water hardness levels of about 115 mg/L as $CaCO_3$ (Tkaczyk, 1982)), which is larger than total NTA concentrations measured (typically about 10^{-5} $\underline{M}$). Hence uncomplexed NTA is not present. Although concentrations of (calcium + magnesium) are approximately 1000 times larger than those of "heavy" metals (e.g copper, nickel and zinc), calcium and magnesium form relatively weak complexes with NTA ($\log \beta_1 = 6.39$ and 5.47 respectively (Martell and Smith, 1974)) compared to copper, nickel and zinc (log β_1 = 12.94, 11.50 and 10.66 respectively (Martell and Smith, 1974)). As a result, soluble copper, nickel and zinc and other "heavy" metals can compete successfully with calcium and magnesium for complexation by NTA.

8. UPTAKE OF NICKEL BY ACTIVATED SLUDGE

This chapter presents the results of experiments undertaken to determine the relevance of free nickel ion concentrations to uptake of nickel by activated sludge. An experiment was also carried out to investigate the mechanisms of nickel uptake.

8.1 NICKEL UPTAKE

8.1.1 Experimental Procedures

Experiments were carried out in the batch mode by adding six 500 mL aliquots of bulk centrifuged (13 000 x g for 10 min) sewage samples to 100 mL of concentrated "stock" activated sludge (see below) in 1 L conical flasks. Increasing amounts of concentrated nickel standard solution were added to five of these aliquots, and the flasks were loosely capped and shaken for 4 h at 200 r.p.m. No ionic strength adjustments were made. The pH was adjusted to 8.0_0 with CO_2 and NaOH and periodically checked during the shaking period. At the end of the shaking period, the supernatant was separated from the sludge by centrifugation (13 000 x g for 10 min) and analyzed for total soluble nickel and free nickel ion concentrations as previously described. Nickel uptake by the sludge was calculated from the difference in total soluble nickel concentrations before and after equilibration with the sludge.

Similar experiments using standard nickel solutions prepared in 0.01 M $NaNO_3$ at pH 8.0_0 were also carried out.

Activated sludge samples were collected from the first pass of the first aeration tank (refer Figure 7.1). Sludge to be equilibrated with standard nickel solutions was washed four times with 0.01 M $NaNO_3$ to remove soluble sewage organics. Sludge samples for the experiments with sewage were washed three times with 0.01 M $NaNO_3$ and once with centrifuged sewage. The first three $NaNO_3$ washing solutions were separated from the sludge by gentle centrifugation (1000 g for 3 min) and decanted. The sludge was concentrated four-fold by compositing during the first two washing steps so that 100 mL aliquots would give MLVSS concentrations of about 1300 mg/L in the equilibration experiments.

The $NaNO_3$ concentration used (i.e. 0.01 M) for sludge washing and the uptake experiments using standard nickel solutions was decided upon after an initial experiment in which sludge samples were washed several times with 0.01 M and 0.10 M $NaNO_3$ solutions. The 0.01 M washing solutions were visually clear after separation from the sludge by centrifugation, whereas the 0.10 M solutions were turbid. This turbidity probably arose from deflocculation of the sludge, a phenomenon which has previously been observed in the presence of high concentrations of cadmium, mercury and zinc (Brown and Andrew, 1972; Neufeld, 1976). Although 0.01 M may be higher than the ionic strength of municipal sewage, washing solutions of this ionic strength were used in order to prevent osmotic shock to the activated sludge.

8.1.2 Uptake from Standard Nickel Solutions

The uptake of nickel by activated sludge from nickel solutions containing no ligands was investigated first to determine whether it was possible to obtain a useful relationship between sludge uptake and soluble nickel. It was expected that in the absence of ligands in solution, the response of the activated sludge towards total nickel and free nickel would be similar.

Ten aliquots containing 0 to 6.81×10^{-5} M (4.00 mg/L) total nickel were shaken with 1300 mg/L MLVSS. Figure 8.1 shows nickel on the sludge, SNi, versus total nickel in solution after equilibration with the sludge, C_{Ni}. These data were non-linear below about 0.4×10^{-6} M total soluble nickel, i.e. those samples that contained less than 5.11×10^{-6} M (0.300 mg/L) total nickel before equilibration with the sludge. Linear regression analyses on the two portions of the plot gave the following values for slopes and intercepts (± 1 standard deviation):

1. Upper part: slope = 5.09 ± 0.02
   intercept = 1.12 ± 0.10
2. Lower part: slope = 7.28 ± 0.41
   intercept = 0.22 ± 0.13

The regression line of best fit for the upper portion had an intercept which was significantly ($p < 0.05$)

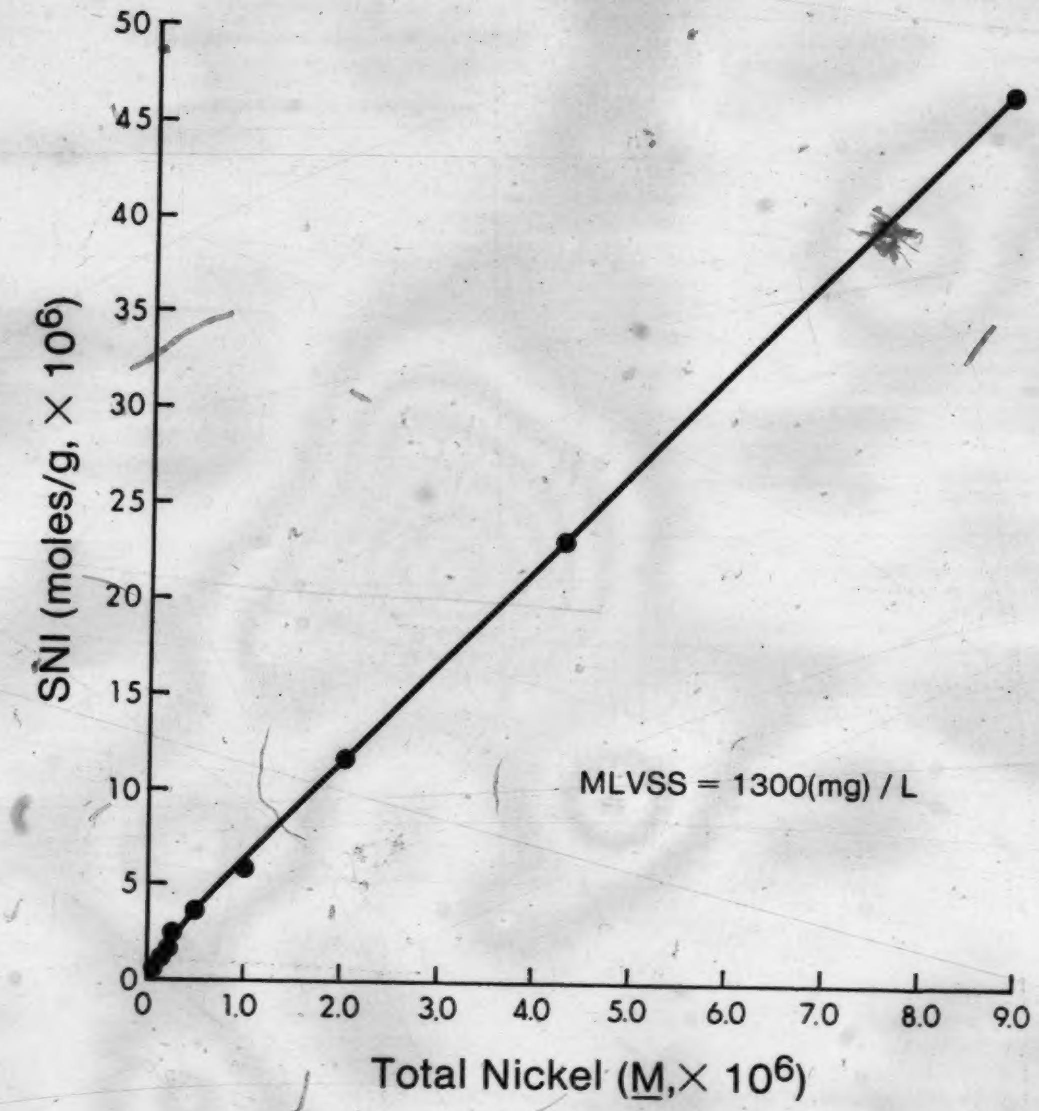


Figure 8.1 Equilibrium Plot of Nickel on Sludge, SNi, vs. Total Soluble Nickel in Standard Nickel Solutions (Experiment 1)

different from zero, whereas that for the lower six data points was not different from zero. Furthermore, the slopes of the two portions were significantly ($p < 0.05$) different from each other.

These results demonstrate that the activated sludge removed a larger fraction of nickel at low than at higher total soluble nickel concentrations. Hence the straight line of best fit for all the data (slope = 5.16; intercept = 0.82) did not accurately describe nickel uptake by activated sludge from samples containing total soluble nickel concentrations typical of municipal sewage.

Nickel removal efficiencies from standard nickel solutions are shown in Figure 8.2. Removals of 87% to 94% were achieved and about 5% greater removal occurred at initial total nickel concentrations less than 5.11×10^{-6} $\underline{M}$ (0.300 mg/L).

Equilibrium plots of nickel on the sludge, SNi, plotted against total soluble nickel and free nickel ion concentrations (C_{Ni} and $[Ni^{2+}]$ respectively) are shown in Figure 8.3. Only data corresponding to the first five points in Figure 8.1 are presented.

The C_{Ni} and $[Ni^{2+}]$ data fitted straight lines with slopes which were not significantly ($p < 0.05$) different from each other (slopes = 7.28 ± 0.41 and 8.51 ± 0.36 respectively). In contrast to the C_{Ni} data, the $[Ni^{2+}]$ data had a y-intercept which was significantly different from zero (0.59 ± 0.05).

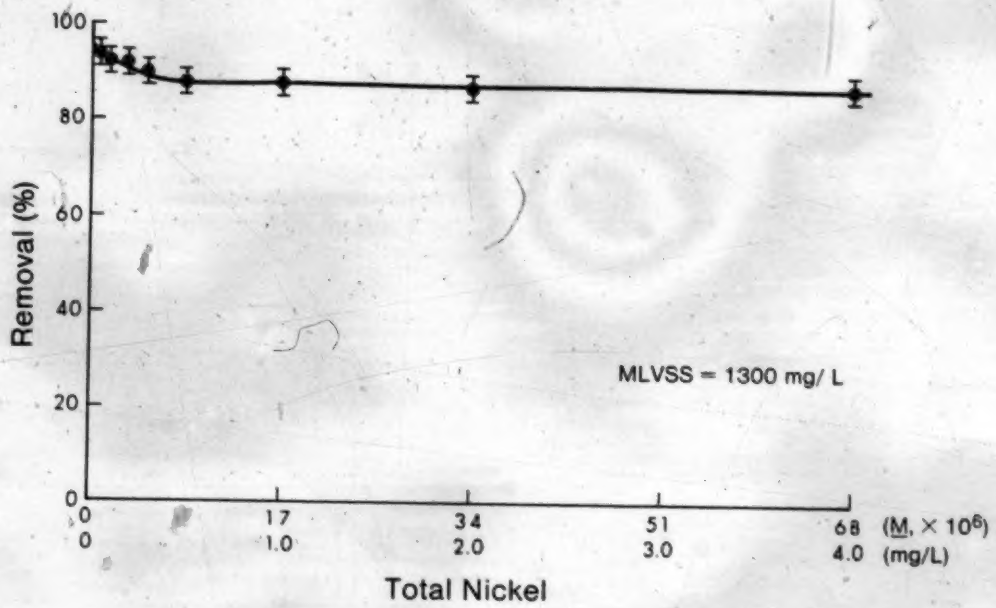


Figure 8.2 Removal Efficiencies of Nickel from Standard Nickel Solutions by Activated Sludge

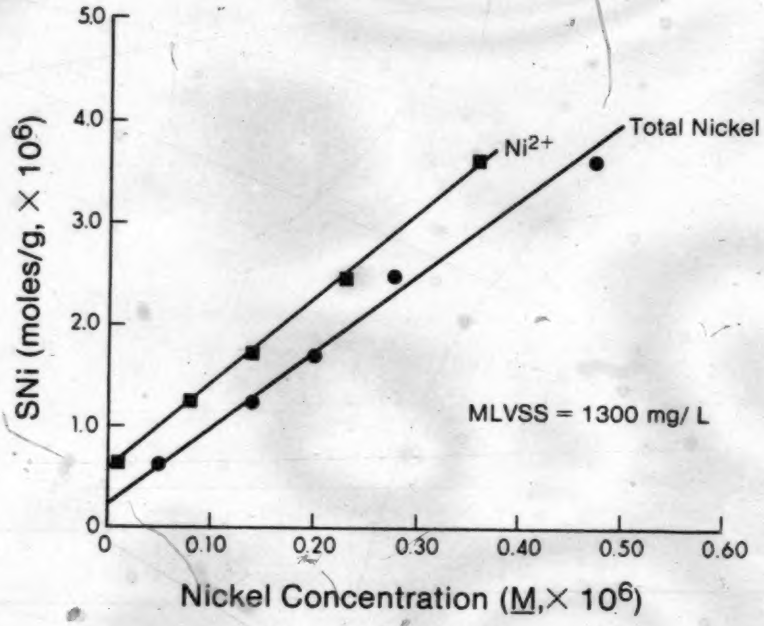


Figure 8.3 Equilibrium Plots of Nickel on Sludge, SNi, vs. Total Soluble Nickel and Free Nickel Ion (Ni^{2+}) Concentrations in Standard Nickel Solutions (Experiment 1)

Although linear relationships between nickel uptake and C_{Ni} or $[Ni^{2+}]$ were expected if Ni^{2+} was the only species taken up by activated sludge, the different positions of the two lines were not. The experiment was repeated using six standard solutions containing 0 to 8.52×10^{-6} $\underline{M}$ (0.500 mg/L) Ni and 1200 mg/L MLVSS in each batch reactor.

Figure 8.4 shows equilibrium uptake isotherms in terms of C_{Ni} and $[Ni^{2+}]$. Similar results to the previous experiment were obtained. Namely, both sets of data were fitted with straight lines of similar slopes (6.72 ± 0.33 and 7.14 ± 0.37 for C_{Ni} and $[Ni^{2+}]$ respectively); the intercept of the C_{Ni} data was not significantly different from zero (0.07 ± 0.13); and the intercept of the $[Ni^{2+}]$ data was not zero (0.39 ± 0.13).

The discrepancy in intercepts between C_{Ni} and $[Ni^{2+}]$ data could possibly be explained by the presence of more than one type of sorption site on the sludge and the release of soluble organics into solution by the sludge. A relatively few metal sites on the sludge with much higher metal affinities than the bulk of the sites would cause the C_{Ni} and $[Ni^{2+}]$ uptake isotherms to have larger slopes at very low nickel concentrations, whereas the slopes at larger nickel concentrations would not change. Consequently, this phenomenon could result in both types of uptake isotherms being displaced upwards. The release of small amounts of soluble organics by the sludge would not affect the $[Ni^{2+}]$ isotherm, but would result in the C_{Ni} isotherm being

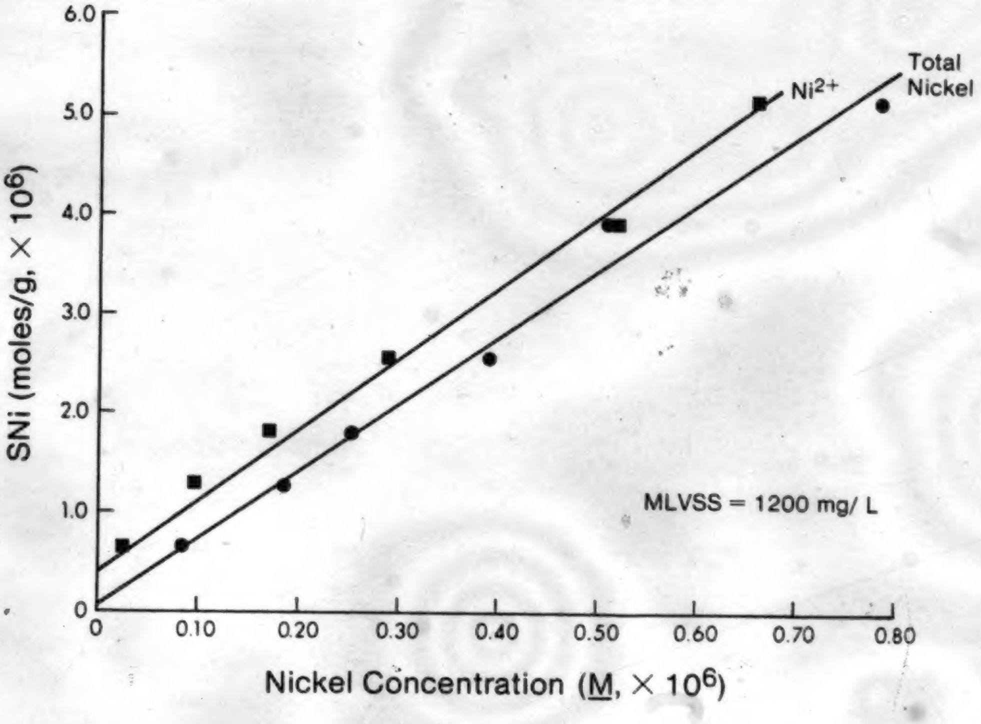


Figure 8.4 Equilibrium Plots of Nickel on Sludge, SNi, vs. Total Soluble Nickel and Free Nickel Ion (Ni^{2+}) Concentrations in Standard Nickel Solutions (Experiment 2)

displaced downwards if these organics complex some of the free nickel present. The net effect of these two phenomena could be for the $[Ni^{2+}]$ isotherm to be displaced upwards to a larger extent than the C_{Ni} isotherm, and this was observed.

8.1.3 Uptake from Sewage

This experiment was carried out on 19-2-82 and 1-3-82 using primary effluent and raw sewage respectively. For each, six aliquots containing 0 to 1.70×10^{-5} $\underline{M}$ (1.00 mg/L) total soluble nickel were equilibrated with 1300 mg/L (primary effluent) and 1600 mg/L (raw sewage) MLVSS. Complexation capacities were also determined for these sewage samples (refer Figures 7.6 and 7.7).

Figure 8.5 shows removal efficiencies of nickel from these samples by activated sludge. In contrast to removals from standard nickel solutions (refer Figure 8.2), nickel removal from sewage increased as the initial total soluble nickel concentrations increased. The removal efficiencies for each sample levelled off when the complexation capacities had been exceeded. Complexation capacities for these samples were 1.1×10^{-5} $\underline{M}$ (0.7 mg/L) and 7.0×10^{-6} $\underline{M}$ (0.4 mg/L) for the primary effluent and raw sewage respectively. The maximum removals from sewage (60%-70%) were much less than those from standard nickel solutions (about 90%), probably because of the presence of weak nickel complexes not measured by the nickel titration technique

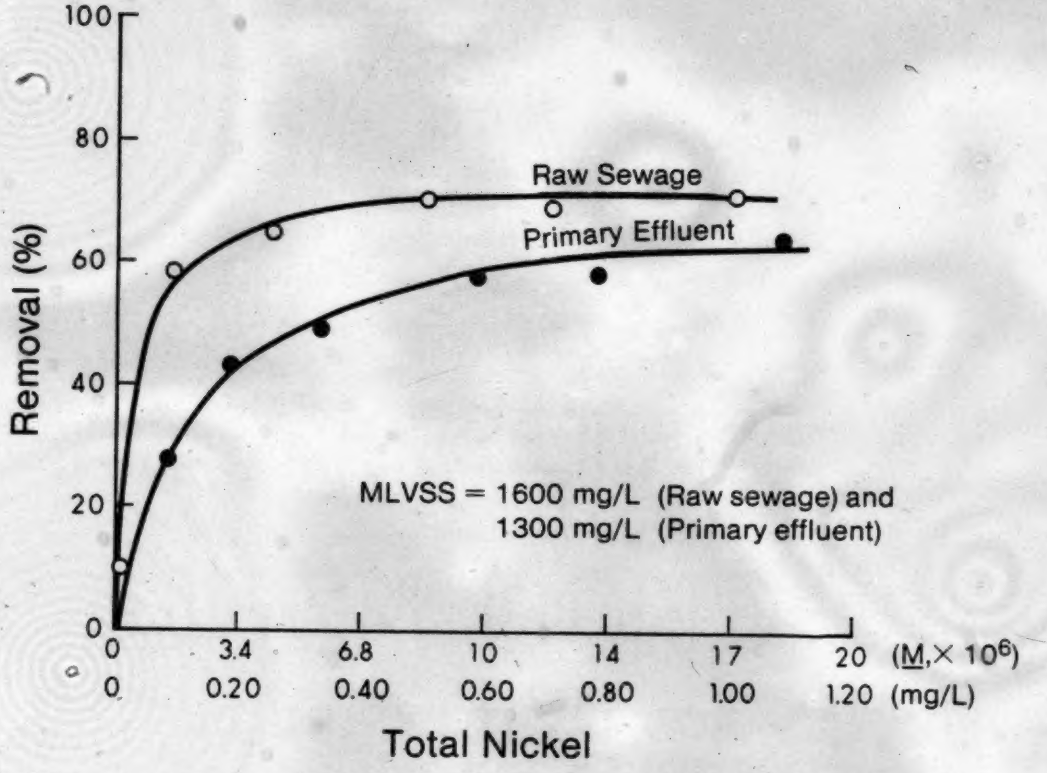


Figure 8.5 Removal Efficiencies of Nickel from Sewage by Activated Sludge

used for sewage (refer Section 7.4.2).

Plots of nickel on the sludge, SNi, versus total nickel (C_{Ni}) and free nickel ion ($[Ni^{2+}]$) concentrations in the supernatant after equilibration with the sludge are shown in Figures 8.6 and 8.7.

There is an obvious difference in the uptake isotherms depending on whether total nickel or free nickel ion concentrations were measured in the supernatant. Isotherms based on C_{Ni} were non-linear over the entire range of nickel concentrations used. The isotherms based on $[Ni^{2+}]$, on the other hand, were linear and had zero y-intercepts. Slopes and intercepts calculated by linear regression were:

1. Primary effluent: slope = 21 ± 1.1
   intercept = 0.19 ± 0.24
2. Raw Sewage: slope = 15 ± 0.78
   intercept = 0.07 ± 0.25

The larger slopes of these isotherms compared with those obtained from the standard solutions (8.51 and 7.14, refer Section 8.1.2) can be attributed to activity coefficient effects and to differences in activated sludge characteristics. Activity coefficient corrections would increase the slopes measured in the standard solutions relative to those in sewage.

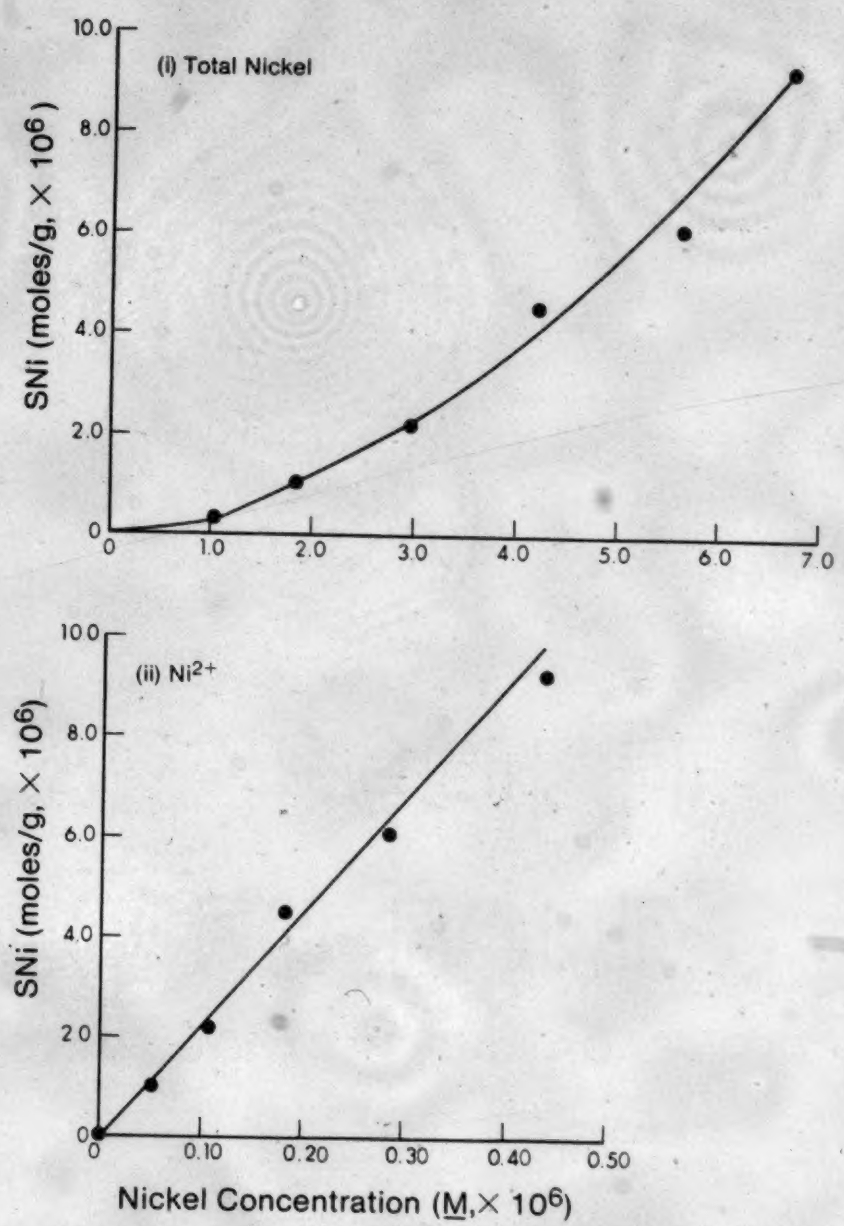


Figure 8.6 Equilibrium Plots of Nickel on Sludge, SNi, vs. Total Soluble Nickel and Free Nickel Ion (Ni^{2+}) Concentrations in Primary Effluent. MLVSS=1300 mg/L (19-2-82)

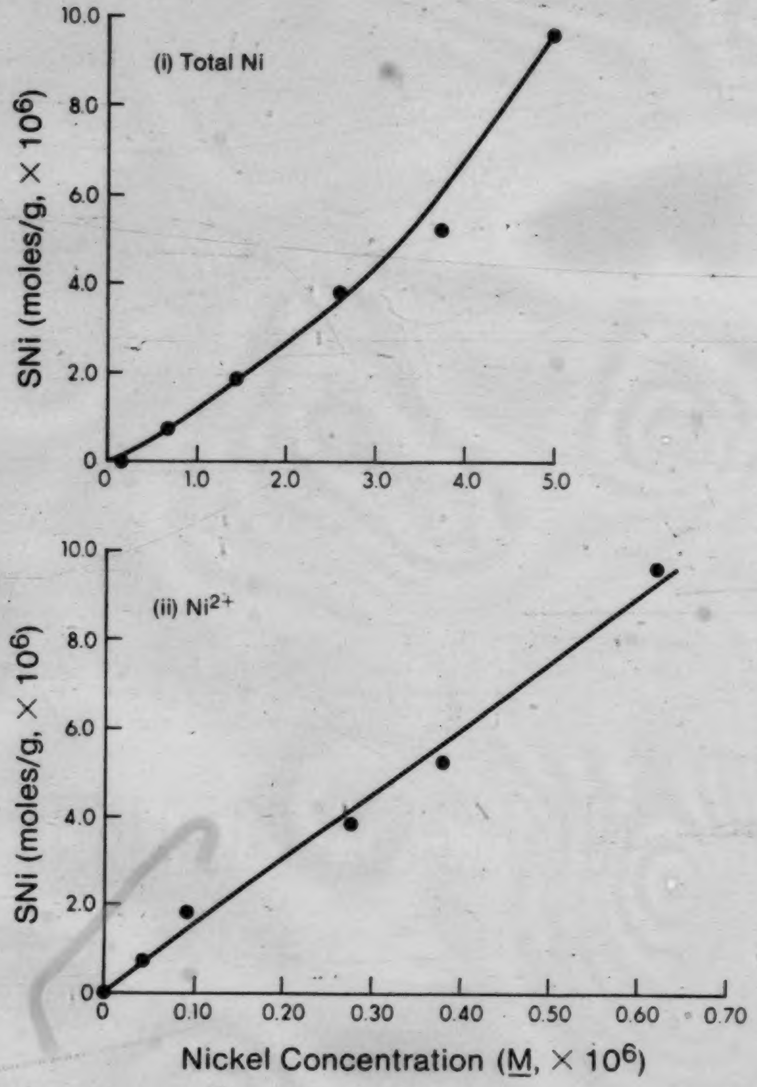


Figure 8.7 Equilibrium Plots of Nickel on Sludge, SNi, vs. Total Soluble Nickel and Free Nickel Ion (Ni^{2+}) Concentrations in Raw Sewage. MLVSS=1600 mg/L (1-3-82)

8.2 MECHANISM(S) OF NICKEL UPTAKE

8.2.1 Rationale

The previous results for nickel uptake from standard nickel and sewage samples by activated sludge clearly show that nickel uptake is directly proportional to the concentration of free nickel ion in contact with the sludge, $[Ni^{2+}]$. Uptake mechanisms involving free nickel ions can be restated as (refer Section 2.1.2.3 and Chapter 3):

1. Ion exchange with exchange sites on sludge, SNa:

$$2SNa + Ni^{2+} \overset{K^{SL}_{IE}}{\rightleftharpoons} S_2Ni + 2Na^{+} \tag{8.1}$$

2. Complexation with charged groups on sludge, e.g. COO^-:

$$2(\text{sludge-COO}^{-}) + Ni^{2+} \overset{K^{SL}_{C-1}}{\rightleftharpoons} (\text{sludge-COO})_2\text{-Ni} \tag{8.2}$$

3. Complexation with uncharged groups on sludge, e.g. L:

$$x(\text{sludge-L}) + Ni^{2+} \overset{K^{SL}_{C-2}}{\rightleftharpoons} (\text{sludge-L})_x\text{-Ni}^{2+} \tag{8.3}$$

The equilibrium constants for these equilibria are:

$$K^{SL}_{IE} = \frac{[S_2Ni]\cdot[Na^{+}]^2}{[Ni^{2+}]\cdot[SNa]^2} \tag{8.4}$$

$$K_{C-1}^{SL} = \frac{[(\text{Sludge-COO})_2\text{-Ni}]}{[\text{Sludge-COO}^-]^2 \cdot [\text{Ni}^{2+}]} \qquad 8.5$$

$$K_{C-2}^{SL} = \frac{[(\text{Sludge-L})_x\text{-Ni}^{2+}]}{[\text{Sludge-L}]^x \cdot [\text{Ni}^{2+}]} \qquad 8.6$$

A sludge distribution coefficient, λ_o^{SL}, can be defined as follows:

$$\lambda_o^{SL} = \frac{[(\text{Sludge})_x\ \text{Ni}]}{[\text{Ni}^{2+}]^*} \qquad 8.5$$

where $x \geq 2$; and

$[\text{Ni}^{2+}]^*$ is the soluble free nickel ion concentration at equilibrium with the activated sludge.

The sludge distribution coefficient, λ_o^{SL}, can be rewritten as follows for each of the uptake mechanisms given in equations 8.1 to 8.3.

1. Ion exchange:

$$\lambda_o^{SL} = K_{IE}^{SL} \cdot \frac{[\text{SNa}]^2}{[\text{Na}^+]^2} \qquad 8.8$$

2. Complexation with charged groups:

$$\lambda_o^{SL} = K_{C-1}^{SL} \cdot [\text{Sludge-COO}^-]^2 \qquad 8.9$$

3. Complexation with uncharged groups:

$$\lambda_o^{SL} = K_{C-2}^{SL} \cdot [\text{Sludge-L}]^x \qquad 8.10$$

It is evident from inspection of equations 8.8 to 8.10 that only the ion exchange mechanism depends explicitly on sample ionic strength.

8.2.2 Experimental Results

The importance of ion exchange as an uptake mechanism for nickel was studied by varying the ionic strength in standard nickel solutions (3.41×10^{-6} M or 0.200 mg/L) from 0.007 to 0.10 M (as $NaNO_3$). These solutions (50.0 mL aliquots) were shaken with activated sludge (1200 mg/L MLVSS) together with 50.0 mL aliquots of corresponding blank $NaNO_3$ solutions. Nickel uptake was determined from the difference in total soluble nickel concentrations before and after shaking with the sludge (refer Section 8.1.1).

As demonstrated for the resin distribution coefficient, λ_o (refer Section 6.3.1.1), a plot of λ_o^{SL} versus $1/[Na^+]^2$ (i.e. $1/\mu^2$) should yield a straight line with positive slope and zero intercept for an ion exchange reaction. Figure 8.8 shows a plot of λ^o_{SL} (± 1 standard deviation) versus $1/\mu^2$. No activity coefficient corrections were made because they could not be made for the sludge phase. The λ_o^{SL} values did not vary significantly for $\mu \leq 0.03$ M, whereas at larger ionic strengths, they decreased.

The results were interpreted to mean that at ionic strengths up to 0.03 M, ion exchange was not the mechanism for nickel uptake. The predominant mechanism is probably complexation of nickel by ligands on activated sludge

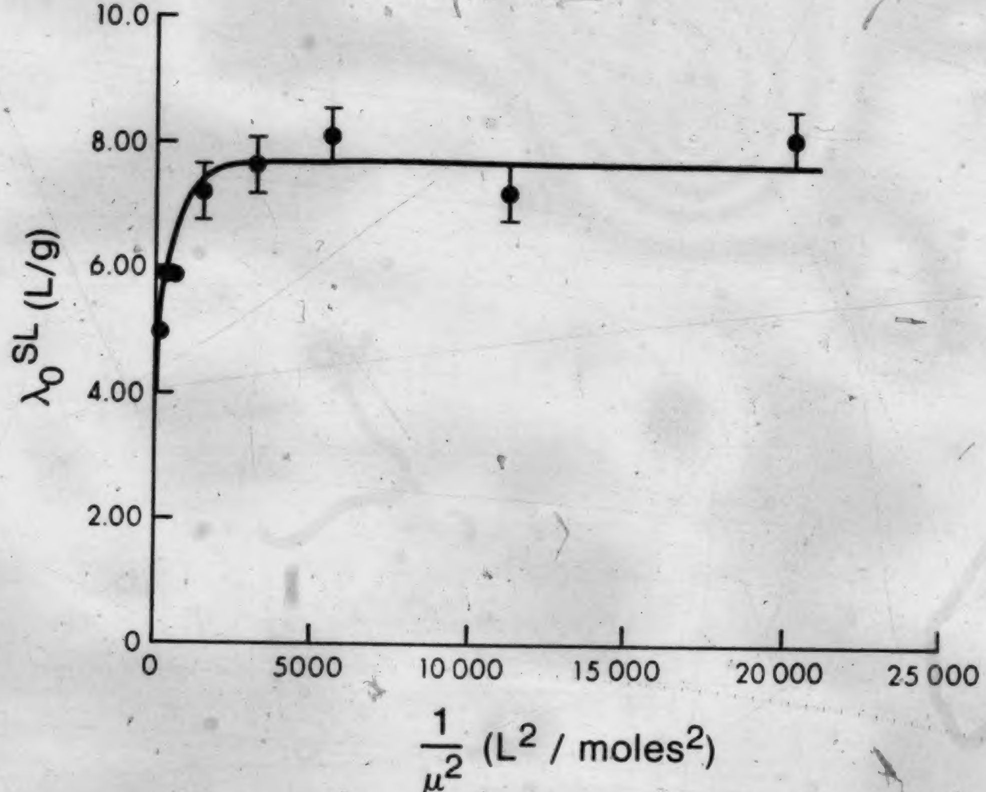


Figure 8.8 Plot of λ_o^{SL} vs. $1/\mu^2$ for Sludge Uptake of Nickel

surfaces. This experiment did not give any information as to the type(s) of complexation reactions which removed soluble nickel from solution.

In addition to ionized carboxyl groups which complex nickel, hydroxyl groups from the large polysaccharide fraction in activated sludge may also complex nickel (refer Section 2.1.2.3). These groups may be only partially ionized at pH 8.0 and hence Ni^{2+} may compete with H^+ ions for uptake. The previous experiment was conducted at a constant pH ($8.0_0 \pm 0.3_0$) and consequently did not provide data about this type of mechanism. Published reports show that metal uptake by activated sludge increases with pH up to values of about 9 (Cheng *et al.*, 1975; Nelson *et al.*, 1981).

9. PREDICTION OF NICKEL REMOVAL BY ACTIVATED SLUDGE

The concepts and conclusions developed in previous chapters can be used to derive equations to quantitatively describe soluble nickel removal by activated sludge in the batch mode. In contrast to previously published models for metal removal (Cheng *et al*., 1975; Nelson *et al*., 1981), the following approach does not require the measurement of nickel-ligand complex stability constants. Hence, assumptions about the number and types of nickel complexes formed in sewage and on the sludge are not necessary.

It has previously been demonstrated (refer Section 8.1.3) that soluble nickel removal is directly related to free nickel concentrations in sewage after equilibration with the sludge. However, the free nickel remaining after sludge equilibration may be less than that in the sample prior to equilibration because of perturbation of nickel complexation reactions in the sewage by the large amount of activated sludge present. This will be true if the sewage is poorly buffered in nickel, and the effect must be taken into account when predicting nickel removal. In order to do this, it is necessary to relate free nickel ion concentrations in the untreated sewage to the corresponding initial complexation capacity curves as obtained by titrating the untreated sewage with nickel (refer Section 7.4.2).

9.1 EQUILIBRIA AND ASSUMPTIONS

Consider the following equilibria of nickel, Ni^{2+}, with ligand, L^-, in the wastewater and with nickel-complexing ligands, S^{y-}, on the sludge:

$$Ni^{2+} + 2L^- \rightleftharpoons NiL_2 \tag{9.1}$$

$$Ni^{2+} + xS^{y-} \rightleftharpoons (S_xNi)^{(2-xy)+} \tag{9.2}$$

The total moles of nickel, T_{Ni}, in a sample of volume, V, containing a known weight of sludge, W, is given by:

$$T_{Ni} = T_{Ni,S} + T_{Ni,SL} \tag{9.3}$$

$$= [Ni^{2+}]\cdot V + [NiL_2]\cdot V \tag{9.4}$$

$$= [Ni^{2+}]^*\cdot V + [NiL_2]^*\cdot V + [S_xNi]^*\cdot W \tag{9.5}$$

where $T_{Ni,S}$ is total moles of metal in the sludge-equilibrated sample solution; and

$T_{Ni,SL}$ is moles of nickel taken up by the sludge.

The superscript (*) refers to metal concentrations in the presence of activated sludge.

The sludge distribution coefficient, λ_o^{SL}, is defined as follows (refer Section 8.2.1):

$$\lambda_o^{SL} = \frac{[S_xNi]^*}{[Ni^{2+}]^*} \tag{9.6}$$

The concentration of nickel taken up by the activated sludge, $[S_xNi]^*$, is calculated from the difference in total soluble nickel concentrations before and after equilibration with the sludge according to equation 9.3.

It is assumed in the following development that λ_o^{SL} has a constant value. This, in turn, assumes that activated sludge characteristics do not vary. As with ion exchange (refer Section 6.1.2), an excess of activated sludge (with respect to nickel sorbed onto the sludge at equilibrium) is also necessary to ensure that λ_o^{SL} is constant.

9.2 DESCRIPTION OF COMPLEXATION CAPACITY CURVES

An idealized complexation curve is shown in Figure 9.1. It has the same shape as those measured in Edmonton sewage (refer Figures 7.2 to 7.7). The complexation curve can be divided into the following four conceptual regions based on the degree of metal buffering (refer Section 6.1.3).

Region 1. A completely buffered linear region. The formal concentration of ligand(s) is much larger than that of nickel and most of the nickel is present as labile complexes.

Region 2. An incompletely buffered linear region. The formal concentration of ligand(s) is much larger than that of the metal, but the metal is not largely present as labile complexes.

Region 3. A poorly buffered non-linear region. The formal concentration of ligand(s) is not in excess with respect to that of metal.

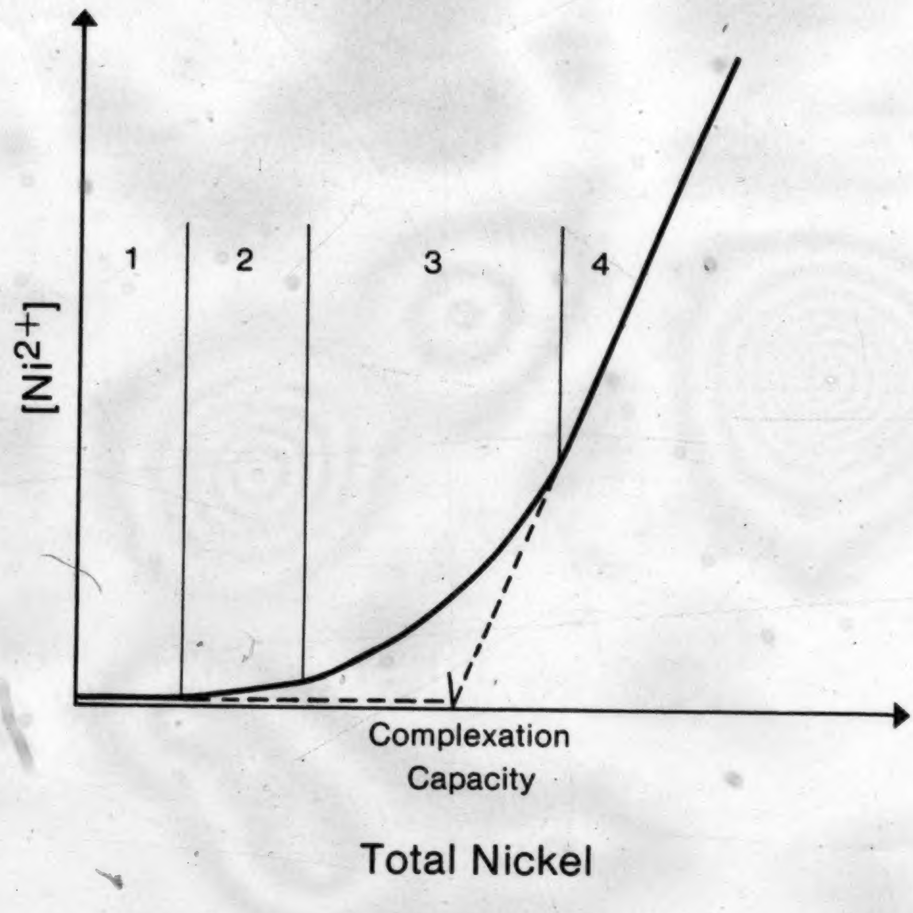


Figure 9.1 An Idealized Complexation Capacity Curve

Region 4. A completely unbuffered linear region. The formal concentration of nickel exceeds that of ligand(s).

9.3 EXPRESSIONS FOR NICKEL REMOVAL

The prediction of nickel removal by activated sludge depends on where the free nickel ion concentration in the untreated sewage occurs on the initial complexation capacity curve. In contrast to the addition of nickel to sewage, the addition of sludge can cause the total soluble nickel concentration to decrease. If the complexation capacity does not change during contact of sewage with sludge, then the total soluble nickel concentration decreases according to the relationship (shape) described by the initial complexation capacity curve.

Metal removal is discussed as follows with respect to the four regions identified in Section 9.2.

Region 1. In this well-buffered region, the nickel taken up by the activated sludge does not significantly alter the free nickel ion concentration present before equilibration with the sludge, $[Ni^{2+}]$, i.e. $[Ni^{2+}]^* = [Ni^{2+}]$. By analogy with equation 6.20, $[Ni^{2+}]^*$ can be related to $[Ni^{2+}]$ as follows:

$$\frac{1}{[Ni^{2+}]^*} = \frac{1}{[Ni^{2+}]} + \frac{\lambda_o^{SL}}{T_{Ni}} \cdot W \qquad 9.7$$

Substitution for $[Ni^{2+}]^*$ from equation 9.6 gives the following expression for nickel taken up by the sludge, $[S_xNi]^*$:

$$\frac{1}{[S_xNi]^*} = \frac{1}{\lambda_o^{SL}\cdot[Ni^{2+}]} + \frac{W}{T_{Ni}} \qquad 9.8$$

The fraction of the total soluble nickel which is initially present as Ni^{2+} (i.e. before equilibration with the sludge), α_{Ni}, is given by:

$$\alpha_{Ni} = \frac{[Ni^{2+}]}{T_{Ni}/V} \qquad 9.9$$

The quantity α_{Ni} is the slope of the initial complexation capacity curve at any total soluble nickel concentration, T_{Ni}/V. Substituting for $[Ni^{2+}]$ in equation 9.8 from equation 9.9 and rearranging gives:

$$\frac{1}{[S_xNi]^*} = \frac{1}{T_{Ni}}\left(\frac{V}{\lambda_o^{SL}\cdot\alpha_{Ni}} + W\right) \qquad 9.10$$

This equation can be further rearranged to give:

$$[S_xNi]^* = \frac{T_{Ni}}{V/\lambda_o^{SL}\cdot\alpha_{Ni} + W} \qquad 9.11$$

Equation 9.11 demonstrates that nickel uptake by activated sludge is related to the slope of the initial complexation capacity curve, α_{Ni}. However, the value of α_{Ni} is negligible in Region 1. Consequently, $(V/\lambda_o^{SL}\cdot\alpha_{Ni}) >> W$, and equation 9.11 reduces to the following form:

$$[S_xNi]^* = \lambda_o^{SL}\cdot\alpha_{Ni}\cdot\frac{T_{Ni}}{V} \qquad 9.12$$

This expression shows that nickel uptake in Region 1 is negligible because the value of α_{Ni} is negligible. Furthermore, an increase in the initial total soluble nickel concentration, T_{Ni}/V, should not cause an increase in nickel uptake by the sludge.

Equation 9.12 can also be derived using equations 9.6 and 9.9.

Region 2. In this incompletely-buffered region, nickel uptake by activated sludge causes the free nickel ion concentration, $[Ni^{2+}]^*$, to be different from that present before contact with the activated sludge, $[Ni^{2+}]$.

The value of α_{Ni} is not negligible and hence sludge uptake of nickel is described by equations 9.8, 9.10 and 9.11. Because the value of α_{Ni} does not vary in this region, there is a linear relationship between nickel uptake and total soluble nickel concentration in the sewage before being contacted with the activated sludge, T_{Ni}.

Region 3. This region is poorly buffered. An analogous expression to equation 6.19 can be derived from the mass balance given by equation 9.5. That is,

$$\frac{1}{[Ni^{2+}]^*} = \left(\frac{V}{T_{Ni}} \cdot \frac{\lambda_o^{SL}}{\lambda^{SL}}\right) + \frac{\lambda_o^{SL}}{T_{Ni}} \cdot W \qquad 9.13$$

where λ^{SL} is defined in a similar manner as the resin distribution ratio, λ (refer equation 6.14).

Substitution for $[Ni^{2+}]^*$ from equation 9.6 and rearrangement yields the following expression for $[S_xNi]^*$:

$$\frac{1}{[S_xNi]^*} = \left(\frac{V}{T_{Ni}\cdot\lambda_o^{SL}} \cdot \frac{\lambda_o^{SL}}{\lambda^{SL}}\right) + \frac{W}{T_{Ni}} \qquad 9.14$$

The ratio $(\lambda_o^{SL}/\lambda^{SL})$ can be shown to equal the inverse of the slope of the initial complexation capacity curve at particular values of T_{Ni}/V. Hence, from equation 9.14:

$$\frac{1}{[S_xNi]^*} = \frac{1}{T_{Ni}}\left(\frac{V}{\lambda_o^{SL}\cdot\alpha_{Ni}} + W\right) \qquad 9.15$$

Although equation 9.15 appears to be the same as equation 9.10, the value of α_{Ni} in equation 9.15 varies. Consequently, $[S_xNi]^*$ in equation 9.15 can be obtained iteratively.

Region 4. The complexation capacity of the sewage has been exceeded and consequently there is a linear relationship between $[Ni^{2+}]$ and T_{Ni} (or C_{Ni} if V remains constant). Under these conditions, $[Ni^{2+}] >> [Ni^{2+}]^*$. For the completely unbuffered case, the slope of the rising part of the initial complexation capacity curve equals unity, i.e. $\alpha_{Ni} = 1$. Hence, equation 9.15 reduces to:

$$\frac{1}{[S_xNi]^*} = \frac{V}{T_{Ni}\cdot\lambda_o^{SL}} + \frac{W}{T_{Ni}} \qquad 9.16$$

Rearrangement of equation 9.16 gives the following expressions for $[S_xNi]^*$:

$$[S_xNi]^* = \frac{T_{Ni}}{V/\lambda_o^{SL} + W} \qquad 9.17$$

$$= \frac{T_{Ni} \cdot \lambda_o^{SL}}{V + W \cdot \lambda_o^{SL}} \qquad 9.18$$

There is also a linear relationship between sludge uptake of nickel and total soluble nickel concentrations in sewage before contact with the activated sludge in this region. Equation 9.15 must be used to predict nickel uptake by activated sludge if the slope of the initial complexation capacity curve is not equal to one.

Cheng *et al.*, (1975) found a linear relationship between nickel removal by activated sludge and initial total nickel concentrations up to about 24 mg/L. The lowest initial total nickel concentration used was 9.9 mg/L, which suggests that the complexation capacities of the synthetic samples used were greatly exceeded.

9.4 PREDICTION OF NICKEL REMOVAL

Data from the two uptake experiments using primary effluent and raw sewage samples (refer Section 8.1.3) were used to test the expressions developed in Section 9.3. Complexation capacity curves for these samples are shown in Figures 7.6 and 7.7, and repeated in Figures 9.2 and 9.3. These figures include the complexation capacity curves measured before and after equilibrium with activated sludge. Both complexation capacities decreased to about one third of their initial values as a result of being shaken with sludge.

Table 9.1 shows the predicted and measured nickel taken up by activated sludge, $[S_xNi]$, for each of the data points

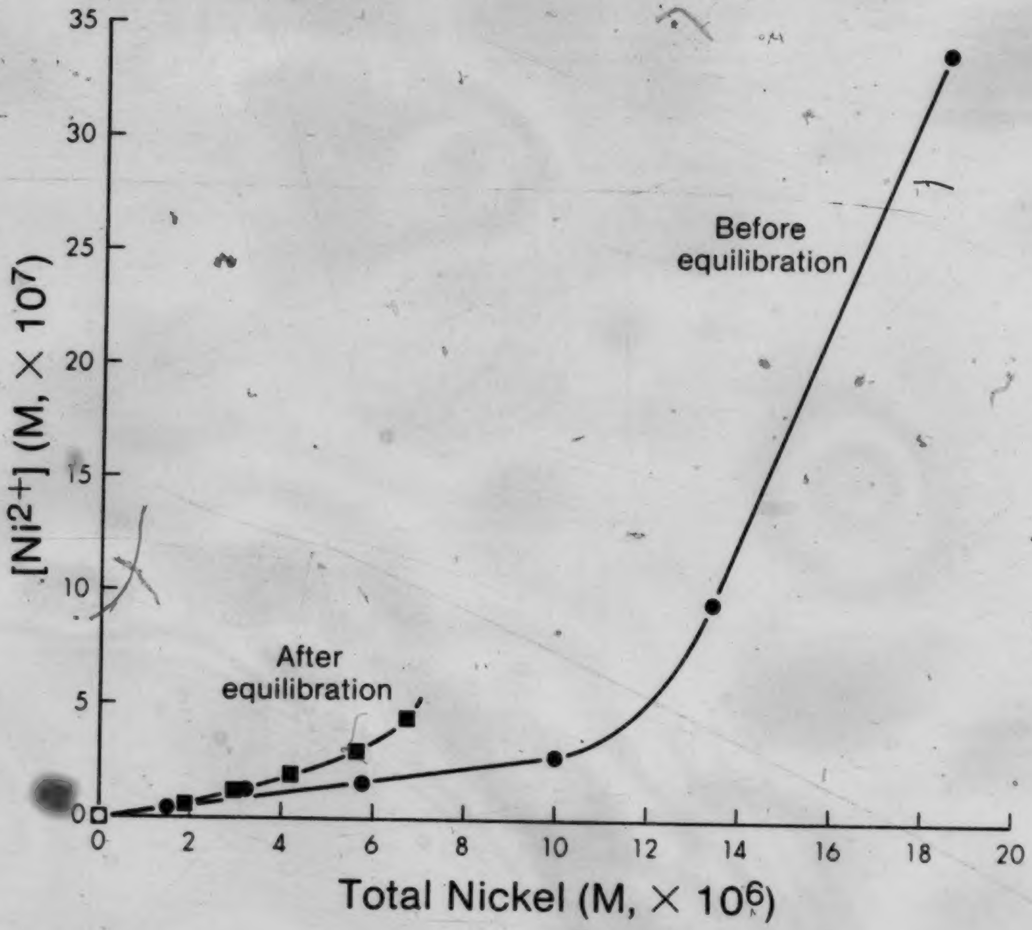


Figure 9.2 Complexation Capacity Curves for Primary Effluent Before and After Contact with Activated Sludge. The open points are before addition of nickel (19-2-82)

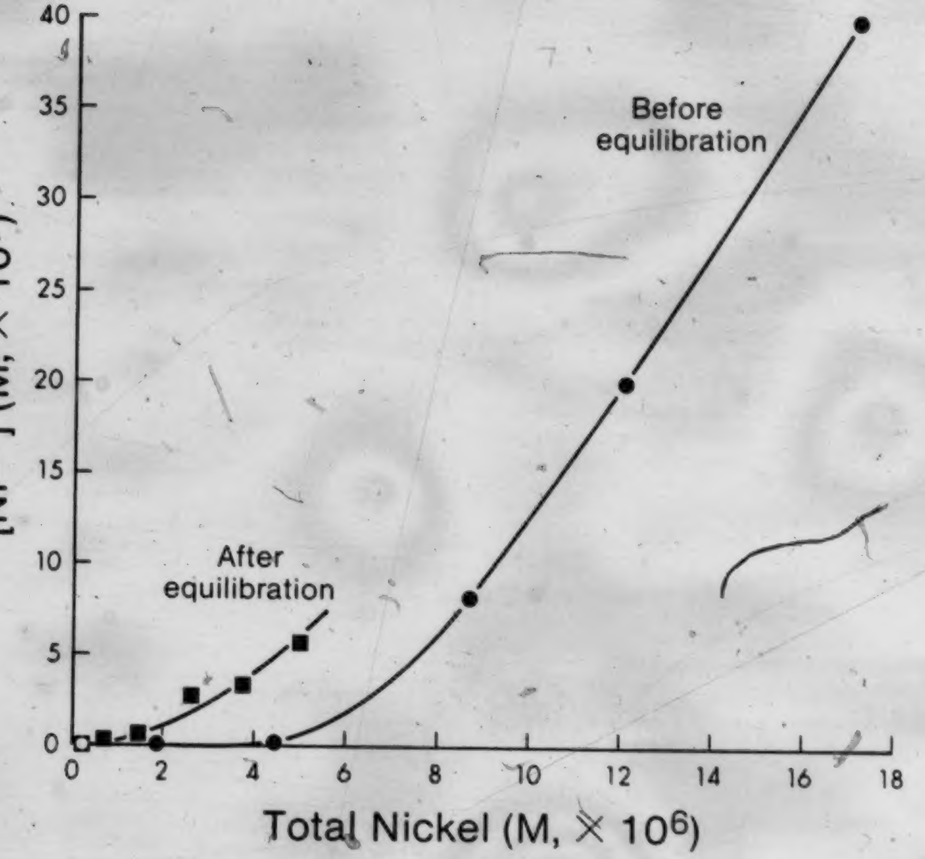


Figure 9.3 Complexation Capacity Curves for Raw Sewage Before and After Contact with Activated Sludge. The open points are before addition of nickel (1-3-82)

Table 9.1 Comparison of Calculated and Measured Nickel Uptake by Activated Sludge

Sample	$T_{Ni}/V^{(1)}$	a_{Ni}	Region	$W^{(2)}$	$[S_xNi]$ (moles/g)		$\frac{\text{Pred. } [S_xNi]}{\text{Meas. } [S_xNi]}$
	($\underline{M}$ (mg/L))			(g)	Pred.$^{(3)}$	Meas.$^{(4)}$	
Primary Effluent (19-2-82)	1.50×10^{-6} (0.088)	0.030	2	0.637	2.71×10^{-7}	3.34×10^{-7}	0.81
	3.20×10^{-6} (0.188)	0.034	2	0.637	6.66×10^{-7}	1.07×10^{-6}	0.62
	5.76×10^{-6} (0.338)	0.027	2	0.637	9.20×10^{-7}	2.21×10^{-6}	0.42
	1.00×10^{-5} (0.588)	0.028	3	0.637	2.01×10^{-6}	4.57×10^{-6}	0.44
	1.34×10^{-5} (0.788)	0.071	3	0.637	2.65×10^{-6}	6.12×10^{-6}	0.43
	1.85×10^{-5} (1.088)	0.183	3	0.637	9.36×10^{-6}	9.29×10^{-6}	1.01
Raw Sewage (1-3-82)	1.70×10^{-7} (0.010)	0	1	0.795	0	1.07×10^{-8}	--
	1.87×10^{-6} (0.110)	0.008	2	0.795	1.04×10^{-7}	7.50×10^{-7}	0.14
	4.43×10^{-6} (0.260)	0.0	3	0.795	2.66×10^{-7}	1.86×10^{-6}	0.14
	8.69×10^{-6} (0.510)	0.099	3	0.795	3.82×10^{-6}	3.82×10^{-6}	1.0
	1.21×10^{-5} (0.710)	0.166	3	0.795	5.12×10^{-6}	5.25×10^{-6}	0.98
	1.72×10^{-5} (1.010)	0.233	3	0.636	9.44×10^{-6}	9.62×10^{-6}	0.98

(1) Total soluble nickel concentration in sewage before equilibrium with activated sludge
(2) Weight of sludge used for each sample aliquot of 600 mL
(3) Predicted
(4) Measured

in Figures 9.2 and 9.3. The value of λ_o^{SL} used was 7.8, which was the mean of the two λ_o^{SL} values previously obtained (refer Section 8.1.2). Volumes, V, of 600 mL were used for all the samples.

With the exceptions of two of the samples, the predicted and measured amounts of nickel taken up by the activated sludge, $[S_xNi]$, agreed to within 60%. These differences can probably be accounted for on the basis of random analytical errors associated with the measurement of total and free nickel ion concentrations (refer Sections 4.3.2 and 6.3.2.3 respectively), as well as errors in determining α_{Ni} values from the initial complexation capacity curves. The largest errors occurred for the points on the early part of the initial complexation capacity curve for raw sewage (refer Figure 9.3). In this region α_{Ni} was negligible and therefore prone to large errors in measurement. Furthermore, the decrease in complexation capacities caused by the activated sludge would probably have caused nickel to become less well buffered during contact of the sewage samples with activated sludge. This would give rise to a systematic error because more nickel would be taken up by the sludge than that calculated using the initial complexation curves.

It should be emphasized that the equations developed to predict nickel removal by activated sludge were tested retroactively using earlier data and not data obtained from experiments specifically designed to test these equations.

Rigorous testing of these equations would obviously require consideration of the sources of error mentioned above. In view of the data used, the predicted and measured nickel uptake results were considered to agree satisfactorily.

10. SUMMARY AND CONCLUSIONS

A major conclusion drawn from the literature review was that despite the large number of studies carried out, the mechanisms and factors which govern metals removal by activated sludge treatment systems do not appear to be well understood in a quantitative or predictive sense. Furthermore, published laboratory studies have usually used considerably higher metal concentrations than those normally found in municipal sewage.

In the present investigation, the removal of nickel by activated sludge was studied by adopting a mechanistic approach. Nickel was chosen as the metal of interest because, in contrast to most other "heavy" metals, it exists predominantly in water soluble forms in municipal sewage and it is poorly removed by biological treatment processes. Typical removal efficiencies for nickel are less than 50%, and are often only about 30%.

It was deemed essential to use natural rather than synthetic sewage and to study removal using a range of total nickel concentrations typical of Edmonton sewage. With this latter criterium in mind, a sampling program was undertaken at the Edmonton Gold Bar Wastewater Treatment Plant to measure the influent concentration range and removal efficiency of nickel relative to cadmium, chromium, copper and zinc.

Although total concentrations of all the metals determined in the influent sewage were higher than those reported for other cities of comparable size in western Canada, nickel concentrations were particularly high. A geometric mean nickel concentration of 0.042 mg/L was found in untreated Edmonton sewage whereas geometric mean concentrations of less than 0.010 mg/L have been reported from Calgary and Vancouver. Hourly influent nickel, cadmium and zinc concentrations did not exhibit distinct diurnal variations, and those for chromium and copper suggested industrial and domestic sources respectively.

Steam heating of sewage and sludge samples acidifed with HNO_3 (1% by volume) for one hour at 15 p.s.i.g. was shown to be the preferred digestion method. Severe nickel and zinc contamination was experienced with the use of acid-washed 0.45 µm membrane filters. Consequently, membrane filtration could not be used to distinguish between soluble and particulate forms of these metals.

Cadmium, chromium and copper were mainly associated with the particulate fraction. A subsequent centrifugation study showed that in contrast to copper, nickel occurred mainly in the soluble fraction. The soluble nature of nickel is consistent with published information that nickel does not readily form insoluble carbonate, hydroxide or phosphate complexes.

With the exception of cadmium, greater removal of metals appeared to occur during primary sedimentation than during the secondary aeration and clarification processes. The overall removal efficiencies for cadmium, chromium and copper were high (81%-90%) whereas those for nickel and zinc were variable and low. These results agreed with published conclusions.

The soluble nature of nickel suggested that nickel might be removed mainly by sorption onto activated sludge surfaces. Possible sorption processes include cation exchange, complexation by charged and/or uncharged ligands on the sludge and adsorption of metal-organic molecules. Consideration of the equilibria for these processes suggested that free nickel ion concentrations were more relevant than total nickel concentrations and led to the postulate that "soluble nickel uptake is primarily dependent on free nickel ion concentrations under equilibrium conditions". The measurement of free metal ion concentrations eliminates the need for some tenuous assumptions which are necessary when quantifying metal uptake by measuring metal-ligand complex stability constants. A major cause of uncertainty concerning the assumptions inherent in the determination of stability constants is the fact that the various ligands present in ill-defined samples, such as sewage, are not known, and consequently, the number and types of complexes formed are not known.

Free nickel ion concentrations were measured by ion exchange using a strong cation exchanger. Cation exchange methods are more sensitive and less prone to interference from other soluble metals and organic matter than anodic stripping voltammetry or ion selective electrode potentiometry. Samples were "swamped" with an inert electrolyte ($NaNO_3$) prior to analysis because this greatly simplifies the method compared to other ion exchange methods. An underlying rationale in choosing ion exchange, together with graphite furnace atomic absorption spectroscopy to determine the uptake of nickel by the resin, was its relatively inherent simplicity combined with high analytical sensitivity and selectivity.

Batch and flow through column equilibration ion exchange methods were investigated. Theoretical equations were derived and experimentally verified using synthetic solutions containing 10^{-4} to 10^{-7} $\underline{M}$ free nickel with glycyl-L-alanine and EDTA as ligands. Both methods provided accurate results. However, the flow through method was easier to use because it is non-perturbing so that each free nickel ion determination required only one sample. Use of the batch method required the analysis of several aliquots of the same sample with different weights of resin to compensate for perturbation of the equilibria by the resin.

The minimum detectable concentration measured with the flow through method of about 4×10^{-9} $\underline{M}$ (0.0003 mg/L) is considerably lower than can be obtained by instrumental speciation techniques in natural waters. The small standard deviation measured at this concentration (RSE = 11%) was caused by "noise" from the graphite furnace atomic absorption spectrophotometer. No fouling of the resin by sewage organics was observed.

The flow through column method was as easy to use with sewage samples as it was with synthetic solutions. A drawback of the method as it currently stands is the large sample volume (500 mL) required. The sample volume can be greatly reduced, while maintaining or improving sensitivity, by decreasing the amount of resin in the column and the volume of eluant used to remove nickel from the resin, and increasing the volume of eluant injected into the graphite furnace of the atomic absorption spectrophotometer (injection volumes of 20 µL were used).

Free nickel ion determinations in Edmonton sewage samples using the batch method gave erroneous results. The atomic absorption signal measured in sewage contacted with resin was enhanced compared to those measured before addition of the resin. This positive interference could not be overcome by the addition of HNO_3 or EDTA to samples or by the method of standard additions. This problem was not encountered with the flow through method, which was used for all free nickel ion determinations in sewage.

Negligible free nickel ion concentrations were measured in untreated Edmonton sewage. The largest concentration (2.9×10^{-8} $\underline{M}$ or 0.002 mg/L) represented only 6% of the total soluble nickel measured in the same sample. Evidently nickel was highly complexed in Edmonton sewage.

Several raw sewage and primary effluent samples were titrated with nickel in order to determine complexation capacities. The sharpness of the "break" in the resulting plots of free nickel versus total soluble nickel concentrations suggested that the major complexing ligands present formed very stable complexes with nickel. The slopes of the rising parts of the titration plots did not approach unity, probably because of the presence of weak complex-forming ligands.

The complexation capacities of all the sewage samples were about 10^{-5} M (0.6 mg/L Ni), showing that the sewage samples contained appreciable excess complexing capacity for nickel. It was demonstrated that gross measures of organic matter, such as total organic carbon, should not be used to determine the concentration of nickel complexing ligands. Concentrations of nitrilotriacetic acid, NTA, were found to be slightly larger than 10^{-5} M, suggesting that NTA could be a major ligand for nickel complexation in Edmonton sewage.

Batch experiments were carried out to relate nickel uptake by activated sludge to total soluble nickel and to free nickel ion concentrations in both standard nickel solutions and sewage samples. The activated sludge (MLVSS = 1300-1600 mg/L) removed 87%-94% of the nickel from standard nickel solutions containing no ligands, and linear sorption isotherms between nickel taken up by the sludge and total soluble nickel or free nickel ion concentrations at equilibrium were obtained.

Different patterns of nickel uptake were observed for sewage samples. Removal efficiencies from sewage increased as initial total soluble nickel concentrations increased, and levelled off when the complexation capacity had been exceeded. The isotherms obtained using total soluble nickel concentrations were non-linear over the entire range of nickel concentrations used (up to 1.7×10^{-5} M or 1.0 mg/L total soluble nickel before contact with the sludge). The isotherms based on free nickel ion concentrations, on the other hand, were linear and had zero intercepts. These results showed very clearly that nickel uptake by activated sludge is directly related to equilibrium free nickel ion concentrations and not to equilibrium total soluble nickel concentrations.

An experiment in which the ionic strength of sewage was varied showed that ionic strengths up to 0.03 M did not affect nickel uptake by activated sludge. This means that varying wastewater characteristics such as hardness and chloride concentration will not have a large effect on nickel removal by activated sludge. Furthermore, the predominant mechanism of nickel uptake was complexation with charged or uncharged ligands on the floc, and not ion exchange.

Equations relating nickel removal to the free nickel ion concentration in untreated sewage and its position on the complexation capacity curve were derived. Predicted nickel uptake by activated sludge was generally consistent with experimental results. Errors in predicted nickel uptake resulted mainly from difficulties in measuring very small slopes to the complexation capacity curves and changes in complexation capacity which occurred when untreated sewage was equilibrated with activated sludge. These equations do not involve measurement of nickel-ligand stability constants. The following conclusions can be made from the equations developed.

1. If the nickel present is well buffered, i.e. largely present as labile complexes, and the formal concentration of ligand is much larger than that of nickel, then uptake is directly related to initial free nickel ion concentrations. Changes in total soluble nickel concentrations do not cause the uptake to alter as long as the buffered conditions are maintained.

2. If the nickel is poorly buffered, i.e. not largely present as labile complexes, then nickel uptake may be linearly or non-linearly related to changing initial total soluble nickel concentrations. The type of relationship depends on whether the initial free nickel ion concentration falls on the linear (incompletely buffered, Region 2) or non-linear (poorly buffered, Region 3) parts of the initial complexation capacity curve.

3. If the complexation capacity is exceeded, total soluble nickel and free nickel ion concentrations are linearly related. Under these conditions, nickel is completely unbuffered if the slope of the rising part of the

complexation capacity curve is unity. Consequently, nickel uptake is linearly related to both total soluble nickel and free nickel concentrations in untreated sewage.

The variable metal removal results described in the literature can be explained on the basis of metal buffering. For example, the direct relationships between metal removal and equilibrium total metal concentrations observed in laboratory studies using high concentrations of metals can be attributed to the complexation capacity having been greatly exceeded in these studies.

The negligible concentrations of free nickel measured in Edmonton untreated sewage mean that these samples were well buffered in nickel. Hence, if these well buffered conditions exist in the aeration basin, it would be expected that negligible amounts of soluble nickel would be removed by sorption to the activated sludge.

However, soluble organics, such as NTA, are known to be biodegraded up to 95% by activated sludge treatment (Woodiwiss *et al.*, 1979). Nitrilotriacetic acid concentrations of 10^{-5} $\underline{M}$ in untreated Edmonton sewage might well be reduced to about 10^{-6} $\underline{M}$ in the aeration basin so that treated sewage becomes less well buffered in nickel. As a result, the amount of nickel removed by sorption to activated sludge surfaces may increase as the complexation capacity is reduced during treatment.

It is appropriate to conclude by presenting reasons why nickel is more poorly removed in activated sludge treatment systems than other "heavy" metals such as copper. The sorption mechanisms and effects of metal buffering that have been found for nickel should also be applicable to copper. Therefore, if sorption was the only metal removal process, these metals should be removed to about the same extent. A major difference between nickel and copper is their physical state in municipal sewage; nickel is mainly in the soluble state, whereas copper is almost entirely associated with particulate matter. As a result, more copper than nickel will be removed by physical processes such as primary sedimentation and enmeshment in the activated sludge floc. Hence, although the free ion is proposed to be the only species relevant to sorption processes for either copper or nickel, sorption processes for copper are masked by the more important physical removal processes.

Overall, the findings of this investigation provide a new method for investigating, and a new basis for quantitatively modelling, metal removal by sorption to activated sludge. This method is easier to carry out, and is free of many of the assumptions which are necessary when using previous methods for predicting removal of soluble metals by activated sludge.

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APPENDIX A. CALIBRATION CURVES FOR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (GFAAS)

Figures A.1 to A.5 show typical calibration curves for cadmium, chromium, copper, nickel and zinc respectively.

Calibration curves for standards prepared in 1% HNO_3 (by volume) are shown for all the metals. For nickel, calibration curves using standard solutions prepared in (0.10 M $NaNO_3$ + 1% HNO_3) and 2 M HNO_3 are also included.

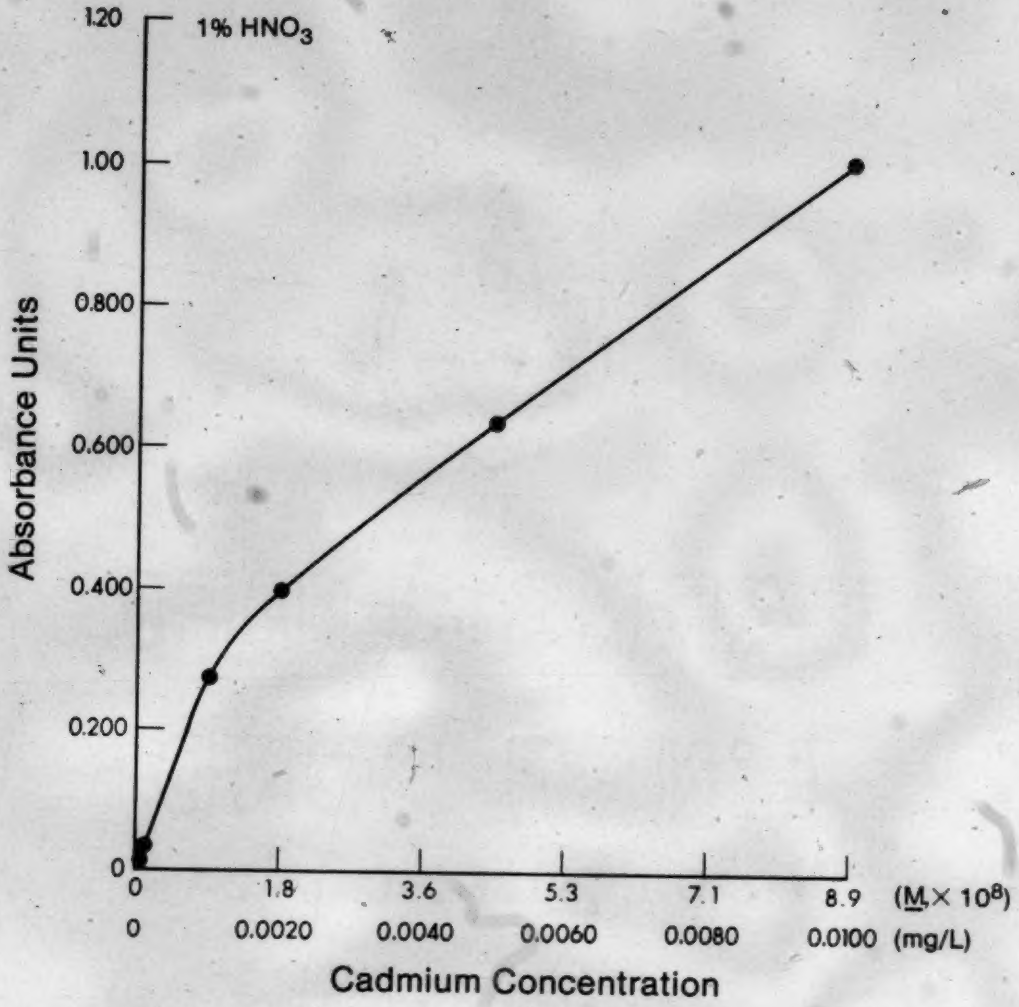

Figure A.1 GFAAS Calibration Curve for Cadmium

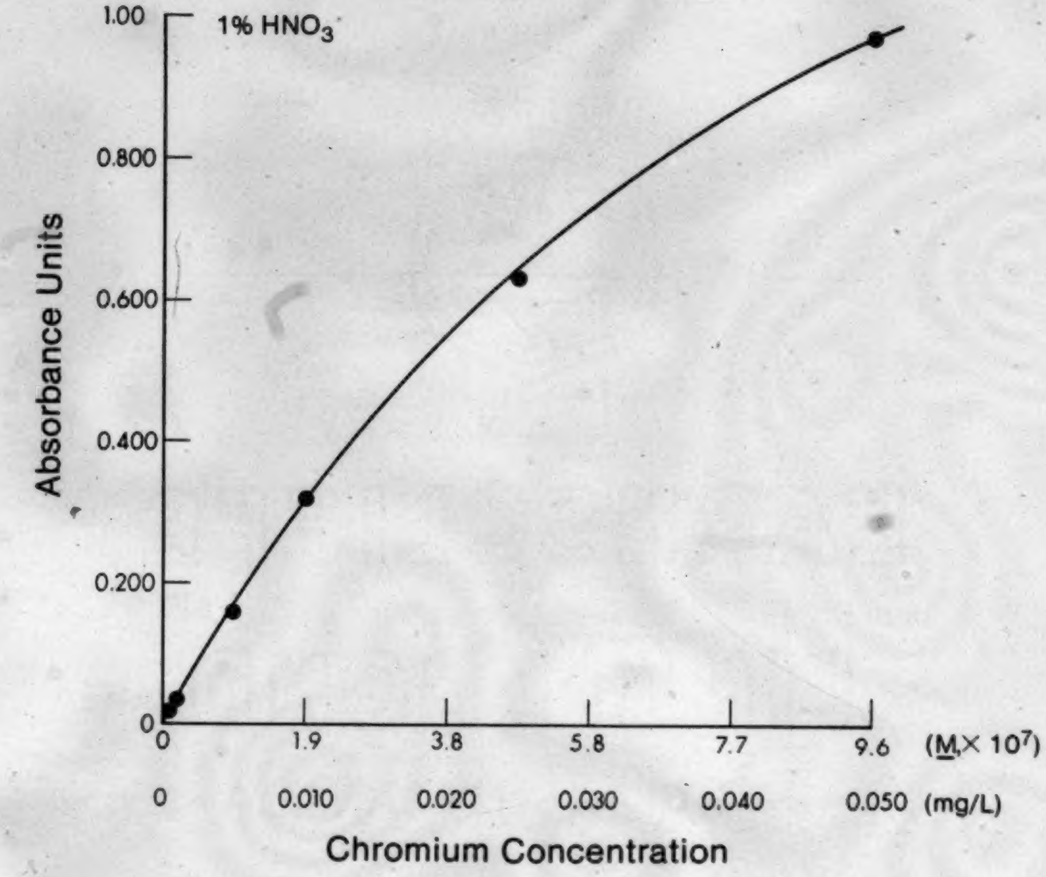

Figure A.2 GFAAS Calibration Curve for Chromium

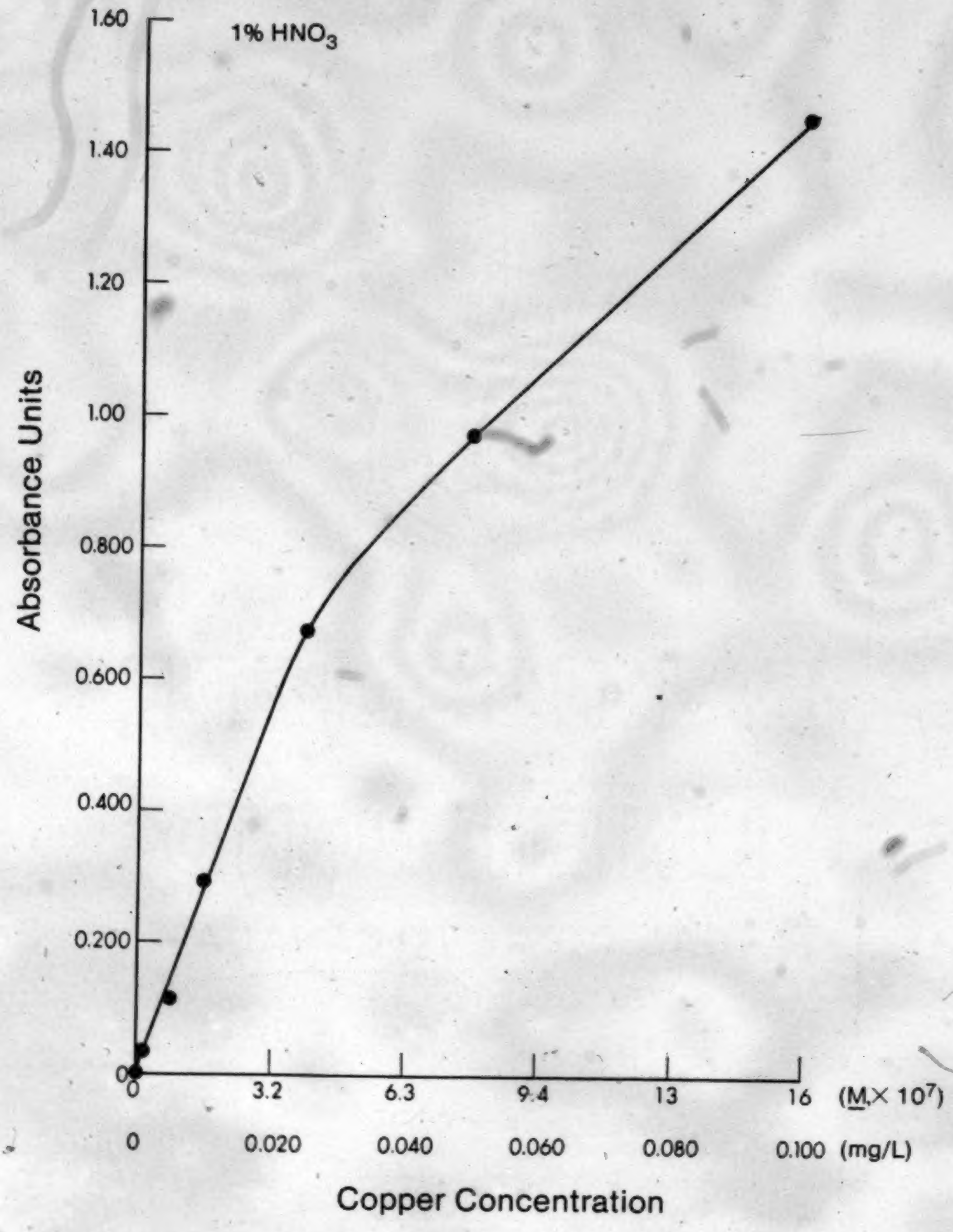

Figure A.3 GFAAS Calibration Curve for Copper

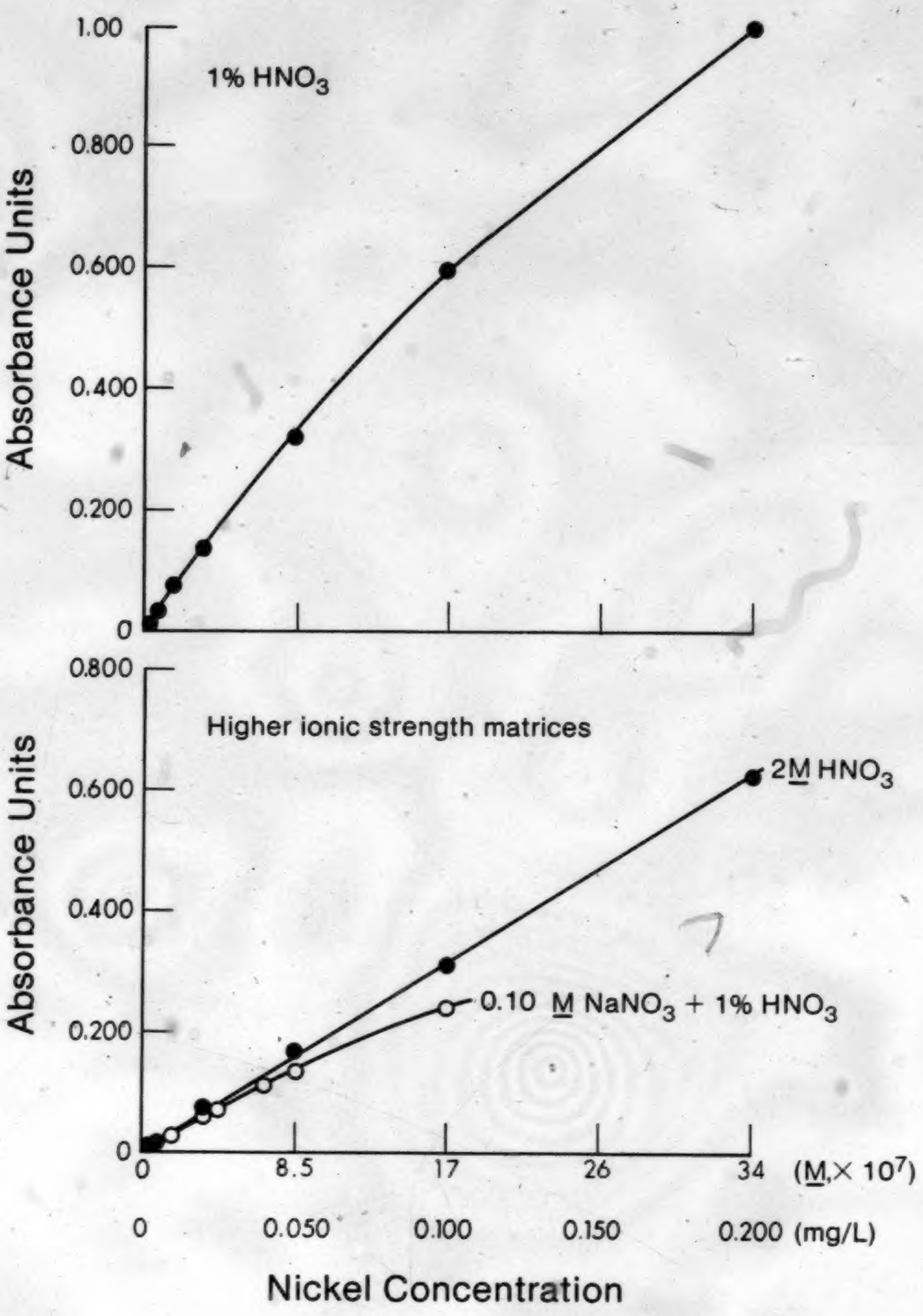

Figure A.4 GFAAS Calibration Curves for Nickel

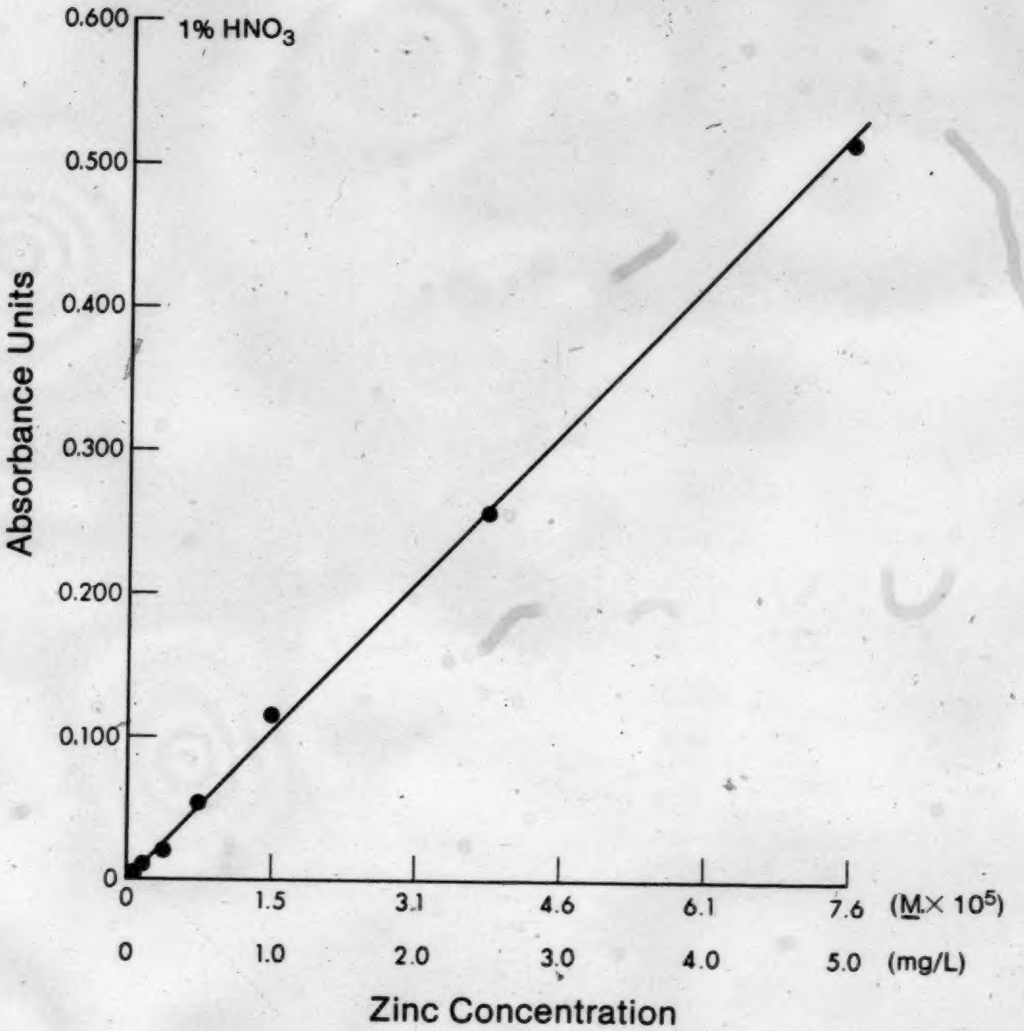

Figure A.5 GFAAS Calibration Curve for Zinc

APPENDIX B. METAL CONCENTRATION AND FLOW DATA MEASURED AT THE EDMONTON GOLD BAR WASTEWATER TREATMENT PLANT DURING JUNE, 1980

Metal concentrations in unfiltered and filtered sewage samples are denoted by the suffixes "-uf" and "-f" respectively.

Raw sewage flows are for the specified individual grit tanks, and are not total influent flows to the plant.

The units used are:

Sewage metals	mg/L
Sludge metals	mg/kg (dry weight)
Flow	ML/d

1 SEWAGE SAMPLES

Date	Hour	Cd-uf	Cd-f	Cr-uf	Cr-f	Cu-uf	Cu-f
Raw Sewage: Right Side Grit Tank (Site A)							
800606	2200	.0038	.0003	.182	.055	.100	.005
800606	2300	.0036	.0000	.334	.099	.095	.002
800606	2400	.0030	.0000	.334	.092	.080	.003
800607	100	.0020	.0006	.413	.166	.090	.006
800607	200	.0040	.0108	.268	.052	.093	.000
800607	300	.0035	.0000	.239	.037	.077	.001
800607	400	.0040	.0003	.276	.031	.068	.010
800607	500	.0046	.0000	.276	.030	.067	.008
800607	600	.0092	.0000	.344	.042	.074	.000
800607	700	.0039	.0001	.256	.052	.061	.007
800607	800	.0036	.0001	.199	.048	.039	.002
800607	900	.0040	.0000	.217	.024	.050	.000
800607	1000	.0039	.0000	.225	.036	.048	.000
800608	1000	.0030	.0000	.217	.020	.043	.000
800608	1100	.0036	.0002	.200	.046	.042	.000
800608	1200	.0031	.0000	.186	.034	.042	.000
800608	1300	.0033	.0002	.165	.015	.063	.000
800608	1400	.0014	.0002	.181	.014	.052	.000
800608	1500	.0016	.0000	.130	.008	.066	.000
800608	1600	.0008	.0002	.140	.016	.057	.000
800608	1700	.0012	.0003	.146	.016	.085	.006
800608	1800	.0034	.0000	.149	.012	.071	.004
800608	1900	.0036	.0000	.161	.014	.054	.004
800608	2000	.0037	.0001	.152	.017	.064	.005
800608	2100						
800608	2200	.0072	.0000	.161	.018	.169	.011
800608	2300	.0033	.0025	.135	.020	.049	.002
800608	2400	.0032	.0000	.126	.018	.068	.007
800609	100	.0012	.0001	.146	.019	.115	.005
800609	200	.0016	.0001	.221	.009	.105	.006
800609	300	.0019	.0003	.199	.012	.099	.005
800609	400	.0043	.0001	.206	.019	.080	.004
800609	500	.0046	.0000	.206	.004	.075	.000
800609	600	.0027	.0005	.271	.015	.082	.011
800609	700	.0029	.0000	.293	.014	.072	.000
800609	800	.0029	.0000	.287	.011	.070	.003
800609	900	.0035	.0001	.670	.038	.110	.000
800610	900	.0026	.0000	.357	.024	.085	.006
800610	1000	.0014	.0001	.407	.052	.104	.001
800610	1100	.0022		1.200		.166	
800610	1200	.0044	.0004	.570	.045	.196	.016
800610	1300	.0056	.0003	3.000	.083	.199	.011
800610	1400	.0065	.0000	.750	.038	.172	.001
800610	1500	.0052	.0000	.500	.018	.139	.009
800610	1600	.0034	.0002	.405	.029	.156	.004
800610	1700	.0030	.0003	.342	.026	.159	.004

Date	Hour	Cd-uf	Cd-f	Cr-uf	Cr-f	Cu-uf	Cu-f
800610	1800		.0004		.039		.009
800610	1900	.0042	.0007	.249	.015		.013
800610	2000	.0038	.0000	.264	.015	.134	.004
800610	2100	.0024	.0002	.238	.020	.147	.002
800610	2200	.0034	.0000	.222	.011	.126	.000
800610	2300	.0026	.0000	.191	.007	.113	.000
800610	2400	.0033	.0000	.202	.006	.108	.000
800611	100	.0024	.0001	.207	.011	.101	.000
800611	200	.0050	.0000	.230	.006	.118	.000
800611	300	.0013	.0000	.140	.011	.069	.000
800611	400	.0030	.0002	.305	.010	.091	.000
800611	500	.0032	.0002	.318	.007	.087	.000
800611	600	.0036	.0001	.303	.005	.082	.000
800611	700	.0033	.0002	.246	.005	.062	.001
800611	800	.0029	.0000	.233	.020	.061	.002
800612	907	.0027	.0000	.499	.031	.057	.003
800612	1007	.0027	.0002	.449	.016	.047	.000
800612	1107	.0046	.0001	4.500	.191	.124	.005
800612	1207						
800612	1307	.0047	.0000	2.500	.120	.122	.002
800612	1407	.0056	.0002	.910	.022	.135	.007
800612	1507	.0057	.0005	.590	.024	.206	.042
800612	1607	.0045	.0003	.437	.018	.177	.005
800612	1707	.0052	.0007	.434	.051	.295	.006
800612	1807	.0073	.0008	.320	.042	.158	.009
800612	1907	.0041	.0006	.266	.051	.167	.012
800612	2007	.0044	.0004	.448	.041	.109	.014
800612	2107	.0009	.0003	.231	.041	.160	.003
800612	2207	.0012	.0000	.150	.032	.070	.005
800612	2307	.0017	.0011	.134	.027	.113	.014
800613	2407	.0011	.0004	.142	.036	.096	.002
800613	107	.0011	.0011	.174	.021	.044	.011
800613	207	.0019	.0004	.164	.020	.041	.006
800613	307	.0019	.0004	.158	.019	.093	.007
800613	407	.0015	.0005	.188	.022	.107	.005
800613	507	.0014	.0008	.166	.009	.084	.006
800613	607	.0016	.0001	.180	.008	.098	.000
800613	707	.0022	.0005	.240	.020	.094	.004
800613	807	.0019	.0000	.210	.030	.080	.008
800614	900	.0021	.0000	.202	.019	.059	.001
800614	1000	.0015	.0001	.156	.036	.061	.000
800614	1100	.0009	.0000	.095	.026	.093	.001
800614	1200	.0019	.0000	.165	.021	.102	.000
800614	1300	.0013	.0000	.159	.018	.087	.001
800614	1400	.0018	.0000	.144	.017	.092	.000
800614	1500	.0014	.0000	.147	.012	.106	.011
800614	1600	.0018	.0000	.183	.029	.118	.009
800614	1700	.0017	.0000	.188	.030	.098	.006
800614	1800	.0018	.0000	.147	.020	.083	.000
800614	1900	.0014	.0000	.167	.017	.096	.003
800614	2000	.0014	.0000	.147	.014	.081	.000
800614	2100	.0012	.0000	.140	.017	.095	.003

Date	Hour	Cd-uf	Cd-f	Cr-uf	Cr-f	Cu-uf	Cu-f
800614	2200	.0013	.0000	.130	.016	.084	.000

Raw Sewage: Centre Grit Tank

800606	1740	.0043	.0007	.550	.033	.139	.022
800606	2200	.0037	.0004	.191	.018	.149	.012
800607	400	.0033	.0006	.211	.052	.095	.011
800607	1000	.0028	.0004	.198	.040	.069	.008
800608	1000	.0028	.0004	.216	.018	.062	.005
800608	1607	.0026	.0006	.133	.015	.106	.009
800608	2200	.0023	.0006	.133	.035	.103	.011
800609	400	.0030	.0003	.147	.024	.094	.004
800609	955	.0036	.0001	.730	.004	.116	.000
800610	900	.0027	.0002	.227	.008	.085	.006
800610	1640	.0056	.0004	.278	.027	.136	.006
800610	2155	.0044	.0012	.230	.014	.130	.008
800611	358	.0044	.0000	.259	.001	.134	.000
800611	900	.0030	.0004	.225	.019	.081	.008
800612	906	.0025	.0003	.270	.025	.078	.009
800612	1600	.0077	.0006	.486	.025	.175	.010
800612	2201	.0027	.0011	.168	.032	.151	.011
800613	400	.0022	.0003	.139	.010	.081	.008
800613	900	.0026	.0004	.449	.020	.068	.006
800614	900	.0022	.0004	.186	.017	.057	.006
800614	1600	.0039	.0007	.225	.029	.104	.011
800614	2203	.0018	.0003	.124	.019	.082	.011

Raw Sewage: Left Side Grit Tank

800610	1641	.0054	.0003	.359	.017	.117	.009
800610	2157	.0050	.0003	.215	.020	.114	.004
800611	400	.0047	.0004	.256	.020	.120	.005
800611	900	.0035	.0005	.224	.013	.068	.009
800612	908	.0032	.0004	.305	.015	.067	.003
800612	1601	.0063	.0006	.415	.033	.196	.009
800612	2202	.0036	.0005	.188	.031	.154	.007
800613	401	.0024	.0002	.141	.018	.078	.008
800613	900	.0032	.0005	.467	.026	.063	.004
800614	902	.0028	.0003	.188	.020	.057	.003
800614	1601	.0045	.0006	.215	.039	.093	.011
800614	2204	.0021	.0000	.117	.000	.068	.000

Primary Effluent

800606	1745	.0046	.0004	.166	.030	.074	.019
800607	516	.0011	.0007	.062	.021	.052	.008

Date	Hour	Cd-uf	Cd-f	Cr-uf	Cr-f	Cu-uf	Cu-f
800608	1634	.0018	.0001	.080	.013	.044	.008
800609	405	.0016	.0007	.037	.013	.034	.015
800610	1644	.0034	.0007	.119	.018	.081	.017
800611	408	.0010	.0008	.037	.014	.036	.020
800612	1642	.0037	.0008	.174	.028	.055	.021
800613	408	.0016	.0004	.054	.013	.030	.015
800614	1606	.0013	.0008	.081	.014	.033	.021
800614	2211	.0023	.0004	.086	.019	.034	.018

Final Effluent

Date	Hour	Cd-uf	Cd-f	Cr-uf	Cr-f	Cu-uf	Cu-f
800606	1756	.0014	.0004	.018	.014	.015	.006
800607	530	.0004	.0003	.028	.022	.009	.007
800608	1644	.0003	.0002	.010	.004	.010	.008
800609	415	.0001	.0003	.010	.005	.008	.006
800610	1652	.0002	.0002	.023	.017	.014	.010
800611	416	.0003	.0003	.020	.007	.014	.007
800612	1623	.0004	.0002	.035	.022	.014	.009
800613	418	.0004	.0003	.020	.018	.011	.009
800614	1615	.0002	.0001	.013	.007	.012	.008
800614	2215	.0002	.0002	.020	.011	.012	.008

Raw Sewage: Right Side Grit Tank (Site A)

Date	Hour	Ni-uf	Ni-f	Zn-uf	Zn-f	Flow
800606	2200	.059	.043	.19	.46	106.7
800606	2300	.083	.037	.15	.35	99.9
800606	2400	.089	.037	.16	.30	95.4
800607	100	.170	.165	.13	.45	90.8
800607	200	.142	.118	.14	.49	84.0
800607	300	.080	.028	.19	.14	74.9
800607	400	.051	.034	.12	.35	65.9
800607	500	.037	.022	.18	.26	59.0
800607	600	.081	.026	.20	.15	54.5
800607	700	.046	.029	.19	.18	54.5
800607	800	.024	.024	.15	.24	52.2
800607	900	.027	.020	.17	.17	56.8
800607	1000	.034	.020	.14	.13	68.1
800608	1000	.028	.047	.14	.13	56.8
800608	1100	.022	.050	.21	.16	70.4
800608	1200	.027	.019	.14	.30	81.8
800608	1300	.053	.040	.16	.16	86.3
800608	1400	.034	.028	.10	.22	93.1
800608	1500	.038	.025	.14	.28	97.7
800608	1600	.036	.030	.21	.20	95.4
800608	1700	.040	.035	.18	.35	88.6

Date	Hour	Ni-uf	Ni-f	Zn-uf	Zn-f	Flow
800608	1800	.041	.034	.15	.12	88.6
800608	1900	.040	.037	.13	.25	88.6
800608	2000	.025	.017	.11	.34	88.6
800608	2100					
800608	2200	.026	.012	.18	.12	90.8
800608	2300	.030	.027	.08	.22	90.8
800608	2400	.034	.051	.08	.37	90.8
800609	100	.025	.014	.13	.25	90.8
800609	200	.041	.057	.18	.15	81.8
800609	300	.034	.032	.22	.15	72.7
800609	400	.032	.017	.17	.15	63.6
800609	500	.040	.025	.14	.39	56.8
800609	600	.033	.020	.21	.29	52.2
800609	700	.037	.018	.20	.10	54.5
800609	800	.036	.016	.17	.15	63.6
800609	900	.054	.026	.25	.25	84.0
800610	900	.043	.019	.17	.00	81.8
800610	1000	.055	.039	.20	.18	93.1
800610	1100	.077		.33		99.9
800610	1200	.050	.044	.42	.24	115.8
800610	1300	.080	.036	.69	.38	113.5
800610	1400	.068	.045	.84	.24	115.8
800610	1500	.055	.046	.50	.25	115.8
800610	1600	.068	.036	.33	.27	113.5
800610	1700	.049	.227	.33	.40	102.2
800610	1800					
800610	1900	.058	.214	.20	.32	99.9
800610	2000	.053	.038	.29	.13	99.9
800610	2100	.057	.130	.22	.48	102.2
800610	2200	.085	.208	.18	.16	102.2
800610	2300	.053	.154	.21	.18	102.2
800610	2400	.034	.148	.17	.24	97.7
800611	100	.038	.183	.17	.28	95.4
800611	200	.067	.135	.23	.17	90.8
800611	300	.019	.211	.18	.16	74.9
800611	400	.070	.189	.64	.15	68.1
800611	500	.042	.208	.22	.62	63.6
800611	600	.037	.176	.24	.19	56.8
800611	700	.024	.239	.18	.40	56.8
800611	800	.029	.090	.15	.13	68.1
800612	907	.051	.123	.15	.09	79.5
800612	1007	.027	.177	.36	.46	95.4
800612	1107	.167	.174	.28	.43	106.7
800612	1207					
800612	1307	.069	.131	.39	.39	111.3
800612	1407	.050	.194	.35	.35	113.5
800612	1507	.091	.244	.39	.38	111.3
800612	1607	.083	.173	.36	.31	109.0
800612	1707	.086	.218	.19	.39	106.7
800612	1807	.080	.276	.18	.72	104.5
800612	1907	.090	.292	.16	.48	104.5
800612	2007	.046	.183	.15	.42	104.5

Date	Hour	Ni-uf	Ni-f	Zn-uf	Zn-f	Flow
800612	2107	.055	.120	.14	.41	99.9
800612	2207	.052	.050	.12	.24	99.9
800612	2307	.058	.052	.13	.26	99.9
800613	2407	.037	.037	.09	.88	102.2
800613	107	.029	.020	.10	.36	95.4
800613	207	.028	.027	.13	.23	88.6
800613	307	.032	.023	.11	.20	77.2
800613	407	.020	.016	.18	.13	68.1
800613	507	.028	.016	.15	.11	61.3
800613	607	.024	.012	.34	.11	56.8
800613	707	.024	.021	.17	.12	61.3
800613	807	.020	.011	.15	.12	70.4
800614	900	.035	.020	.15	.11	56.8
800614	1000	.022	.019	.13	.12	68.1
800614	1100	.027	.017	.10	.10	74.9
800614	1200	.034	.020	.16	.09	86.3
800614	1300	.045	.027	.21	.21	95.4
800614	1400	.018	.035	.18	.16	102.2
800614	1500	.029	.021	.18	.15	102.2
800614	1600	.038	.032	.18	.17	102.2
800614	1700	.037	.048	.18	.25	99.9
800614	1800	.027	.021	.53	.20	97.7
800614	1900	.015	.035	.12	.27	97.7
800614	2000	.021	.038	.12	.26	97.7
800614	2100	.016	.047	.10	.24	97.7
800614	2200	.024	.014	.12	.29	95.4

Raw Sewage: Centre Grit Tank

800606	1740	.203	.178	.52	.90	104.5
800606	2200	.101	.038	.30	.29	106.7
800607	400	.076	.052	.23	.24	65.9
800607	1000	.052	.030	.15	.13	68.1
800608	1000	.041	.031	.28	.24	56.8
800608	1607	.045	.039	.27	.55	95.4
800608	2200	.034	.122	.27	.28	90.8
800609	400	.019	.016	.27	.28	65.9
800609	955	.045	.019	.22	.40	88.6
800610	900	.036	.032	.27	.17	77.2
800610	1640	.081	.036	.40	.32	111.3
800610	2155	.084	1.720	.35	.15	102.2
800611	358	.057	.092	.33	.28	70.4
800611	900	.032	.105	.21	.12	79.5
800612	906	.044	.136	.21	.13	72.7
800612	1600	.300	.220	.42	.24	113.5
800612	2201	.076	.245	.30	.43	99.9
800613	400	.030	.023	.30	.15	72.7
800613	900	.026	.017	.29	.14	72.7
800614	900	.033	.032	.21	.13	54.5
800614	1600	.039	.031	.24	.18	102.2

Date	Hour	Ni-uf	Ni-f	Zn-uf	Zn-f	Flow
800614	2203	.043	.022	.28	.28	97.7

Raw Sewage: Left Side Grit Tank

800610	1641	.068	.046	.45	.28	111.3
800610	2157	.100		.40	.05	102.2
800611	400	.048		.56	.22	70.4
800611	900	.027		.32	.15	79.5
800612	908	.033		.25	.12	72.7
800612	1601	.240		.50	.37	113.5
800612	2202	.074	.378	.34	.29	99.9
800613	401	.022	.020	.24	.11	72.7
800613	900	.032	.024	.26	.11	72.7
800614	902	.029	.052	.24	.10	54.5
800614	1601	.037	.031	.26	.10	102.2
800614	2204	.028	.019	.24	.25	97.7

Primary Effluent

800606	1745	.649	.025	.28	.18	299.8
800607	516	.045	.038	.13	.13	172.6
800608	1634	.025	.025	.25	.11	272.5
800609	405	.016	.016	.14	.33	188.5
800610	1644	.038	.037	.21	.21	327.0
800611	408	.017	.326	.24	.20	204.4
800612	1642	.118	.280	.17	.17	313.4
800613	408	.015	.038	.18	.27	215.7
800614	1606	.015	.038	.16	.14	293.0
800614	2211	.017	.037	.15	.15	277.1

Final Effluent

800606	1756	.543	.035	.58	.38	240.7
800607	530	.146	.138	.19	.19	170.3
800608	1644	.039	.039	.25	.18	240.7
800609	415	.021	.021	.19	.19	190.8
800610	1652	.025	.025	.19	.15	227.1
800611	416	.018	.412	.14	.14	199.8
800612	1623	.020	.334	.12	.24	202.1
800613	418	.028	.041	.14	.12	197.6
800614	1615	.030	.029	.31	.10	204.4
800614	2215	.033	.031	.13	.11	204.4

2 SLUDGE SAMPLES

Date	Hour	Cd	Cr	Cu	Ni	Zn
Mixed Liquor						
800606	1750	18.3	658	195	47	383
800607	520	183.2	715	257	198	924
800608	1638	17.3	715	166	140	445
800609	410	12.8	674	208	65	432
800610	1647	11.2	834	215	76	587
800611	411	12.5	781	240	68	549
800612	1636	18.2	841	246	105	333
800613	411	12.7	751	229	96	296
800614	1611	163.5	857	283	125	365
Return Sludge						
800606	1756	16.2	935	276	84	884
800607	526	15.2	846	278	119	759
800608	1642	12.5	813	187	118	725
800609	413	13.0	787	271	130	708
800610	1650	12.4	877	185	113	612
800611	415	13.0	829	239	97	632
800612	1627	14.2	1021	190	102	535
800613	416	12.4	886	245	93	545
800614	1614	12.5	980	264	121	557
Primary Sludge						
800606	1806	13.9	1195	225	71	669
800607	530	32.0	1047	254	75	626
800608	1650	17.4	1010	261	168	707
800609	422	14.3	913	320	176	671
800610	1656	13.6	960	302	121	692
800611	422	11.2	1057	1586	92	740
800612	1616	12.1	1350	228	71	833
800613	423	11.9	1281	334	103	777
800614	1623	13.3	1910	961	117	773
Digested Sludge						
800606	1810	204.2	991	363	58	691
800607	540	23.1	1054	284	62	765
800608	1655	21.5	1208	286	88	672
800609	430	21.5	1152	194	80	664

Date	Hour	Cd	Cr	Cu	Ni	Zn
800610	1705	67.0	1183	254	76	652
800611						
800612	1620	25.5	1152	189	91	724
800613	426	19.8	1166	233	82	734
800614	1620	19.2	1236	310	115	675